







THE COLLOID CHEMISTRY  
*of the*  
SILICATE MINERALS





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VOLUME I

THE COLLOID CHEMISTRY  
*of the*  
SILICATE MINERALS

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## GENERAL PREFACE

The field of agronomy has broadened substantially in recent years. Concurrently there has developed a greater measure of specialization in many of its sub-fields. The profession of agronomy is well served in the matter of elementary and general text-books but is not adequately supported by more advanced treatises. Comprehensive reference books in the former German tradition filled a useful place in bringing together all relevant information on particular subjects, but English-speaking scholars have infrequently shown inclination towards their preparation. Instead, a monographic form of treatment has much to recommend it. There is in every research field a certain stage of growth that must be accomplished before the preparation of a monograph is feasible. The main features must be recognizable and clear. At this stage, however, the preparation of a monograph may facilitate the further development of the subject and accelerate the researches that must be accomplished. The preparation of a critical review may, therefore, be an important step in advancement of knowledge.

Several years ago the American Society of Agronomy appointed a Committee on Monographs to inquire into the need for monographs in the field of agronomy and, if desirable, to arrange for their publication. During the war years little progress could be made, but it is now anticipated that a number of subjects in soil science and plant science relating to crops can be treated authoritatively in monographs. The authors will be selected from among those who are directly contributing to the development of the respective subjects. It is hoped that this series will contribute to the advancement of the field and profession of agronomy.

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February 1949



## PREFACE

An inescapable dilemma faces the writer of any monograph which deals with materials having both scientific and commercial importance. As Samuel Butler wrote in his Notebooks, "Everything must be studied from the point of view of itself, as near as we can get to this, and from the point of view of its relations, as near as we can get to them. If we try to see it absolutely in itself, unalloyed with relations, we shall find, by and by, that we have, as it were, whittled it away. If we try to see it in its relations to the bitter end, we shall find that there is no corner of the universe into which it does not enter." Each author, then, must make his own compromise of these disparate ends.

I have deliberately chosen to restrict this work, in the main, to evidence obtained from the study of reasonably pure materials; well aware, that by so doing, diverse and important applications have been relegated to the background. In the present state of our knowledge of the colloidal minerals it is, in my opinion, more important to clarify the fundamentals than to describe the technical detail of applications. This restriction conforms to my own predilections in research, and enables me to lay before the reader an account, from the viewpoint of a participant, in which the advances of the last twenty years are especially emphasized.

My experiences, as I have taken part in this rapid and significant yet unspectacular progress, have been wholly delightful. In so far as I have been able to judge, this field of work has been free alike from competitive over eagerness and from sterile controversy. Mineralogists, colloid chemists, soil scientists and ceramists have all contributed. Each has been interested in what those in different fields were doing. Hence duplication of effort has been rare, and the rapid progress made has been due in no small measure to the general overriding of traditional subject matter boundaries. My hope, in writing this monograph, is that it will prove of value in showing the strength, weaknesses and extent of the foundations which we have jointly laid.

The restriction of subject matter which I have adopted has eased considerably the burden of references. This is especially the case in Chapter 11 which deals with ionic exchange. Much fundamental work in this field has been concerned with substances which are either not colloidal minerals (permutites, mixed hydrous oxide gels, exchange resins) or are not well defined chemical entities (whole soils). I have therefore limited this chapter to a sketch of the present outlook upon theory as it bears upon the exchange reactions of the colloidal minerals themselves. In a similar way Chapter 13 presents a brief sketch of our present ideas on viscosity, thixotropy and plasticity before taking up the very limited information on well

defined systems. A considerable technical literature on relatively poorly defined systems is thus by-passed.

The author is grateful to Dr. Wm. A. Albrecht, Chairman of the Department of Soils, to the Dean of the College of Agriculture, to the President and Board of Curators of the University of Missouri for the granting of summer leave in 1946 when much of the writing of this monograph was accomplished. It is a pleasure also to express appreciation of the cheerful readiness with which Mrs. Lorene Burton, our secretary in the Department of Soils, dovetailed the typing of the manuscript into her varied duties. Mr. James E. Spencer, formerly a student in the College of Engineering, was responsible for the redrawing of the graphs and the diagrams.

I am indebted to Dr. Bryon T. Shaw and the publishers of Soil Science for permission to reproduce the electron micrographs here presented as figures 26 and 27; to Dr. Shaw and the publishers of the *Journal of Physical Chemistry* for figures 38, 79 and 80; and to Dr. Shaw and the Soil Science Society of America for figures 28 and 29. Prof. W. A. Hynes of Fordham University read the manuscript at the instance of the publisher, and by his careful attention to detail uncovered a number of minor omissions, etc., which have now been rectified.

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February 1949

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## CHAPTER 1

### HISTORICAL OUTLINE

The progress of the last twenty years has transformed the study of the colloidal silicates from an almost hopeless empiricism to a well integrated part of mineralogy, colloid chemistry, soil science, ceramics, and even of civil engineering. It would be difficult nowadays to find a better example of the way in which the elucidation of chemical structure has acted as a catalyst upon diverse applications. One can see also, as more becomes known about structure, how the emphasis changes and the impetus of the more fundamental investigations is directed toward behavior and its interpretation. The general direction of future advances can now be discerned. The further unfolding of structural detail will proceed side by side with extensive studies of properties, and it is safe to predict that the applications will ramify greatly.

Several circumstances combine in making the recent history of the colloidal silicates unusually intricate. In the first place two of the oldest constructive human activities, agriculture and pottery making, are deeply concerned with their properties; so much so, that in modern times experimental stations and research institutes have concentrated attention upon them. Under these auspices it is natural that every effort should be made to interpret behavior in terms of application. Since, however, the latter, in absence of sound knowledge of chemical structure, is severely limited in range, there arose a strong demand for structural information. Where none was forthcoming, substitutes were invoked. Thus, prior to the advent of X-ray studies, so-called structural formulae for the silicates were propounded which were entirely speculative. No chain of logical reasoning, such as the organic chemist uses, could be devised in their support. On the other hand, while structure remained so grossly speculative, many preferred to seek analogies; to interpret the behavior of the clays, for instance, in terms of that of simpler chemical systems having properties in common with them. In this way some stressed the analogy between the clays and the permutites, others that between the clays and the zeolites, still others that between the clays and mixtures of hydrous oxides. In any case it was a dangerous choice, as those of us who look back can now see.

Among the mineralogists, less concerned with applications, interest in the clays was spasmodic. The great advances in mineralogy in the nineteenth century came about through the development of consistent methods for describing the morphology and optics of crystals, combined with greater

precision in chemical analysis. The mineralogist's ideal silicate was a multifaceted crystal showing a combination of forms, from which a precise axial ratio could be deduced. At the same time, the chemical formula should comprise integral molecular proportions of constituent oxides. Many instances of departures from this ideal gradually accumulated. For the most part, however, they were cases in which a variable chemical composition was combined with a relatively constant crystal morphology. They could therefore readily be explained in terms of Mitscherlich's concept of isomorphism. The clays not only showed wide variation in composition, but their morphology remained almost entirely indeterminate.<sup>1</sup> For the most part the clays remained in a kind of mineralogical back-water. Hosts of mineral names accompanied ill-characterized samples in the collections of the larger museums. The writers of mineralogical texts, obviously ill at ease, skipped over the whole group with scant mention. Even now the only detailed account to be found in a general mineralogy is that of Dufrénoy in his "*Traité de Minéralogie*" (2nd Ed., Paris, 1856). It is worth reading today since one vitally important conclusion stands out above the rudimentary yet peculiarly modern classification and the obsolete names. It is clear that Dufrénoy recognized differences in macroscopic properties between different groups of the clays. Viewing his work from the modern angle, one can see that the colloidal nature of most clay minerals does not completely obliterate their separate and distinctive properties.

This observation brings us to comment upon the part played by the colloid chemists in clay research. As late-comers upon the scene they benefited by the accumulated experience of earlier workers. Again, viewing the matter in retrospect, one can now see how frequently they overemphasized the similarities of all extensive interfaces and failed to recognize the connection between surface atomic structure and colloidal properties. This situation has finally corrected itself, but not before many of those concerned with applications, grasping eagerly at this new branch of chemistry, had tried to explain all the peculiarities of the clays in terms of their extensive surface.

The enormous advantage which macroscopic crystallinity confers may well be illustrated by a comparison of our knowledge of the zeolites and of the clay minerals as it appeared about the year 1920. On the basis of external morphology and optics, the zeolites were already classified. They were known to differ from other hydrous silicates in two ways: firstly, by their continuous dehydration curves; secondly, by their property of base exchange. In both these cases the external morphology remained

<sup>1</sup> In one instance only have microscopic crystals of a clay mineral been measured on a goniometer. Miers in 1888 described the morphology of a crystalline kaolin-like clay discovered by Dick in Anglesey. This clay has since been renamed dickite.

the same, but the optics showed appropriate changes. Many syntheses of the zeolites under conditions believed to be similar to those which produced them in nature had been performed. All this was known, in spite of the fact that the zeolites were relatively scarce minerals of no commercial importance. In contrast, the clays, ubiquitous upon the surface of the earth and utilized industrially in enormous quantities, were classified less clearly in 1920 than by Dufr  noy in 1856. The microcrystalline kaolins only could lay claim to partial characterization. Clays differing in properties from the kaolins were generally assumed to contain amorphous impurities. Base exchange was not known to be an important property of any named clay minerals, although the soil chemists had early recognized its association with unidentified silicates present in many soils. The submicroscopic fractions of the different clays were widely assumed to be amorphous, the word "colloidal" being generally used synonymously. Differences in thermal behavior were known to exist, but how far these could be ascribed to mineralogical differences, and how far to variations in the colloidal character, remained a matter of conjecture. No syntheses of the clays had been performed.

This state of affairs was certainly not due to neglect. The bibliography of the clays up to 1920 was already much more extensive than that of the zeolites. It must be ascribed in large measure to the urgent need for new, or more searchingly applied, methods of attack, especially for those which would aid in deciding questions of purity. Once materials of reasonable purity have been characterized a most important step has been taken. Such characterization, however, is practically impossible for insoluble solids like the silicates unless some of the properties of crystalline material are present, and unless samples from different sources can be quantitatively compared. Thus we find interwoven in the story of clay chemistry since 1920 five main lines of investigation: the search for natural clays of high purity, the development and improvement of methods of fractionation and characterization, the search for evidences of crystallinity, the combining of various lines of evidence to throw light upon ultimate atomic structure, and finally, the use of structure to explain new properties and to suggest new applications. This sequence is no different from that followed by organic chemists in the study of various natural products; it is indeed the classic procedure. The colloidal character of the clays made its application more involved than usual, threw much more strain upon methods of identification, but the basic steps remained the same. No single person, no one laboratory, carried through all of them. The work was piecemeal, individualistic, governed in the 1920's by a wide variety of objectives, and intermingled with much that was later seen to be irrelevant.

The first major work which led directly to the heart of the problem of

clay constitution was agricultural in ultimate objectives and colloid-chemical in techniques. It was favored by the peculiar postglacial conditions under which a broad belt of soils in the Middle West of the United States was formed. R. Bradfield (1923), concerned with the intractable nature and the acid character of the subsoils in large areas of northern Missouri, set about fractionating these acid clays by centrifugal methods. He then characterized the fractions by potentiometric and conductometric titration curves, and by measurements of cataphoresis, comparing them with mixed gels of silicic acid, aluminum hydroxide, and iron hydroxide of the same composition (2, 3). It was shown that below a certain particle size these clay fractions resembled each other very strongly, but none of them behaved like mixed gels of hydrous oxides. It seemed as though a clay acid was a major constituent in the heavy subsoil, of which the Putnam soil provided a particularly good example. Thus was the doctrine of reactive silicates in the soil, which had been suggested by Thomas Way in 1850, and spasmodically supported by many later workers, reborn. One may inquire why this should have been necessary.

During the period from 1900 to 1920, when colloid chemistry underwent its spectacular growth, attention was repeatedly called to the fact that adsorption could cause inert materials with extensive surfaces to simulate acids. Since soils and clays certainly contained material with extensive surfaces they presumably would be able to adsorb acids and so to acquire acidic properties. The nature of the adsorbed acids was not closely specified, but in the case of soils the decomposing organic matter was presumed to supply adequate quantities. Bradfield's experiments, conducted on clays with a very low content of organic matter, disproved this hypothesis and showed that the acidity was an inherent property of the clay, which should therefore be regarded as a colloidal acid in its own right. Subsequently the new technique of electrodialysis was used to purify these colloidal acids by removing the exchangeable or adsorbed cations still held under natural conditions.

A very different approach to the problem appeared in a little-known, but brilliant, paper by P. Koettgen in 1921 (17). This investigator applied the heavy liquid technique of the sedimentary petrologist to a series of clays from geological formations in northern Germany. Instead of using organic liquids, however, he employed aqueous thallium formate solution, hastening the separation by a powerful centrifuge. He was able to secure valid fractionations of several clays, and to show that the fractions differed both in composition and in properties. Some appeared to be identical with kaolinite, while others, of lower specific gravity, were more acid-soluble and contained chemically combined alkalis and alkaline earths. Thus, it appeared that even mixed clay materials were not experimentally hopeless.

About the year 1924, the U. S. Geological Survey assigned C. S. Ross to work on clay deposits, some of which, the bentonites, were beginning to find new uses in industry. These, therefore, formed the subject of the first paper by Ross and Shannon (28). The bentonites are rocks formed by the deposit of volcanic ash in lakes or seas. They show a wide range of stages of decomposition of volcanic glass to form clays. The latter were examined both *in situ* by thin section methods, and after separation of the coarse accessory minerals from aqueous suspension. It was shown that these clays have, *in situ*, a high birefringence and are therefore crystalline. On dispersion in water, however, particles too small for optical identification by standard methods predominate. The bentonites often consist of a single clay, admixed with small amounts of coarse accessory minerals readily removed by sedimentation. The predominant mineral is usually montmorillonite, less commonly beidellite. Ross and Shannon, by combining accurate chemical analyses with refractive index determinations, were able to make the distinction between these clays and those of the kaolin group much clearer than heretofore. They provided clear evidence that even these highly colloidal clays were essentially crystalline. That they should become noncrystalline simply by dispersion in water was obviously implausible.

Two years later, Larsen and Steiger (18) applied similar methods to a series of clays which appeared to range in composition from beidellite, with little iron, to nontronite, a hydrous silicate often previously considered as the iron analogue of kaolinite. They showed that nontronite was more closely akin to beidellite than to kaolinite and established the fact that a continuous series of members with intermediate compositions exists between the two end members. Thus, it appeared that montmorillonite, beidellite, and nontronite were all closely related in properties, being readily distinguished from the kaolinite clays by their much greater uptake of water vapor at various humidities, by their higher content of silica, and by their distinctive optical constants.

About the same time, attempts were being made to determine whether clay suspensions from other sources contained crystalline material or not. Zocher, a colloid chemist, had shown how certain optical effects due to the orientation of nonspherical particles in a rotating liquid could be used in a qualitative way to test this matter. Kaolinite particles, as would be expected, showed these effects. The author, in 1926, repeated this experiment with fine clay material from the Rothamsted soil and showed that much crystalline material was undoubtedly present (19). Two years later a quantitative method was devised in which the birefringence resulting from electrical orientation was accurately measured. The first clay to be investigated in detail was Bradfield's Putnam, all fractions of which were

shown to be crystalline. These quantitative measurements, however, went considerably farther. It was shown that below a certain particle size, this clay, prepared from a subsoil, was essentially homogeneous, just as Bradfield had demonstrated chemically. Most important of all, the birefringence showed a measurable variation with the nature of the exchange cation indicating that, in this clay, the sites for base exchange were internal and related to the anisotropy of the crystal in some definite way. This variation with the exchange cation was absent in the case of kaolinite, a clay of low exchange capacity, whose ionic exchange could thus be ascribed to external surfaces only. These experiments were published in 1930 (20).

During the years 1926 to 1930 evidence of the crystallinity of colloidal clays from soils was accumulating in several other laboratories. At the First International Congress of Soil Science, held in the United States in 1927, Ross asserted that soil clays generally were probably crystalline to a much greater extent than had previously been supposed (29). Allen, in 1930, made the very specific statement that many Midwestern soils contained the mineral beidellite (1).

In 1930 and 1931 also, two papers dealing with the application of X-ray methods to soil colloids appeared. That by Hendricks and Fry (10) contained, in addition to X-ray evidence based on comparisons of soil clays with known clay minerals, a study of thin films obtained by drying clay suspensions upon a microscope slide. These films often provided interference figures, indicating a considerable degree of particle orientation in the plane of the flakes. The paper by Kelley, Dore and Brown (16) also gave X-ray evidence of crystallinity of soil clays, and introduced for the first time a method of investigation which, in succeeding years, was to provide a considerable array of misleading conclusions. This was the technique of fine grinding, which we shall consider in detail in Chapter 9. As a whole, the X-ray investigations on soil clays gave, at this time, considerable promise of achieving quantitative estimates of the different minerals present. Further work, however, revealed unexpected difficulties, and although considerable progress has been made by Nagelschmidt, Jackson, and others, it is still not quantitative in all cases.

In the year 1930, L. Pauling published two epoch-making papers on the X-ray diffraction produced by minerals with a highly micaceous cleavage (27). The following were investigated; gibbsite ( $\text{Al}_2(\text{OH})_6$ ), brucite ( $\text{Mg}_2(\text{OH})_6$ ), cristobalite ( $\text{SiO}_2$ ), the micas, the chlorites, pyrophyllite, talc, and kaolinite. He showed that all these minerals, chemically so different, gave a unit cell in the plane of cleavage approximating to  $5.1 \text{ \AA}$  by  $8.8 \text{ \AA}$ , the agreement being particularly good for gibbsite and cristobalite. Hence, he was led to consider all these as sheet or layer structures, the units being cristobalite, gibbsite, or brucite sheets. Thus, kaolin was given an un-

symmetrical structure with one silica and one alumina layer combined in a single unit three oxygen layers thick. In pyrophyllite two silica layers were combined with a central alumina layer giving a unit four oxygen layers thick. This same unit, with appropriate substitutions, served also to explain all the diverse compositions found in the whole mica group.

Thus, in 1930 it became apparent that X-ray methods might be used in two ways in clay investigations: to provide data which could be interpreted in terms of chemical structure, and to aid in identification by precise characterization. This second aspect formed an important part of detailed studies of the kaolin clays and of halloysite and allophane published in 1931 and 1934, respectively, by Ross and Kerr (30, 31).

Based on Pauling's suggestions, further work on structure rapidly followed. Gruner (9), in 1932 and 1933, suggested structures for the three isomeric members of the kaolin group, kaolinite, nacrite, and dickite, all of which have the ideal composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . The differences between them are due to differing displacements of the silica layer relative to the alumina layer.

In 1933 was published the first successful attempt to assign a structure to montmorillonite. Hofmann, Endell and Wilm, in Berlin, made very careful comparisons of montmorillonites with pyrophyllite (12). The spectra were identical except for a single line near the axis of the X-ray beam. In pyrophyllite this line had a fixed position and was regarded as a reflection from planes at right angles to the  $C$  axis; that is, it afforded a measure of the  $C$  axis, or the spacing characteristic of the thickness of the unit sheets. In montmorillonite this line lay much closer to the central beam, its angular deflection being so small that it had been missed by the earlier workers. Thus, it appeared that montmorillonite had the same type of layer lattice as pyrophyllite, both giving the characteristic spacings in the plane of cleavage  $a = 5.1 \text{ \AA}$ , and  $b = 8.8 \text{ \AA}$ . This innermost interference, however, in the case of montmorillonite changed its position with water content, thereby clearly proving, since the other lines remained fixed, that it was caused by planes parallel to the cleavage, whose distance apart varied with the water content of the clay. The pyrophyllite structure plus this variable spacing was therefore assigned to montmorillonite. Shortly afterwards beidellite was also found to give this variable spacing (13). A curious situation was then revealed. The idealized formula for montmorillonite and beidellite was  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . The chemical analyses, on the other hand, indicated that the former approximated to  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$  and the latter to  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . Hofmann, Endell and Wilm allowed for the presence of magnesium in montmorillonite by assuming that it replaces part of the aluminum in the gibbsite sheet, but they did not account satisfactorily for the composition of beidellite, or for exchangeable bases



found in appreciable amounts in both clays. The basic features of their structure have, however, been generally accepted as correct and, as we shall see later, many conclusions drawn from it have been verified by experiment.

It was natural, therefore, that efforts should be made to find other lines of evidence bearing upon structural features. The author's examination of a series of carefully fractionated clays afforded such an opportunity (21). These had been subdivided according to particle size, using a newly devised quantitative method. The fractions were thus accumulated for study. They were examined optically, their base exchange properties were studied, and finally, they were analyzed chemically. Two of these clays, a bentonite and a Putnam clay subsoil, appeared to be homogeneous in the finer fractions. They were all crystalline; the former appeared to be identical with the mineral montmorillonite and the latter with beidellite. In each case the cation exchange capacity was practically independent of particle size, and the substitution of one cation for another caused a measurable change in the birefringence as determined by electrical orientation. All the evidence, therefore, X-ray, physical, and chemical, placed montmorillonite and beidellite in the same group, and one could see that the great stumbling block to a general understanding of these reactive clays lay in the apparent discrepancy between the X-ray and chemical formulae. The author, therefore, devised a procedure for the examination of the chemical analyses which could be used in two ways. If certain plausible replacements were assumed to operate—Al for Si in the silica layers, Mg for Al and Fe for Al in the gibbsite layers—then the Ca, Na, K, and other exchangeable cations could be regarded as balancing the negative charges induced by the Al for Si or Mg for Al substitutions. Thus all the bases present, exchangeable and non-exchangeable, could be accounted for. The exchangeable bases were assigned to the variable spaces between the silicate units, in agreement with the optical evidence and with the very minor increase in exchange capacity with diminishing particle size. If the new Hofmann, Endell and Wilm structure were assumed to be correct, it then appeared that beidellite was the member in which the replacement was Al for Si, whereas in montmorillonite Mg for Al predominated. However, the matter could be examined in another way. It was possible, using these replacements as variables, to calculate what lattice types would fit the analyses. In many cases these extended over a considerable range. Thus, for many montmorillonites the possible ratio of silica layers to alumina layers could be varied from 2:1 to 4:1. The Hofmann, Endell and Wilm ratio of 2:1 was thus only one of several chemically feasible. However, when the extensive analyses of Ross and Shannon were examined in this way, only a single ratio, namely 2:1, was found to be common to the montmorillonites and beidellites. Since all other evidence placed them in the same group, this could be taken as

strongly confirming the operation of the above replacements and the assignment of the exchange cations in association with water molecules to the spaces between the silicate sheets.

The great advantages of this theory were soon realized. It received strong support from Gruner's X-ray work on nontronite (8), which also showed the variable spacing. It served as a basis for the monumental survey of the montmorillonite group more recently completed by Ross and Hendricks (32). Further, as we shall see later, it has aided greatly in explaining the transformation upon drying of certain exchange cations to the nonexchangeable form.

Thus, although the X-ray evidence taken by itself was insufficient to provide a completely detailed proof of atomic arrangement, it clearly set limits to the possible variations. The chemical and physical evidence has consistently supported the general correctness of the Hofmann, Endell and Wilm structure as interpreted by the present author in 1935.

In the years following 1930 rapid advances were made in the recognition and structural elucidation of other clay minerals. Thus, Mehmél (26) examined halloysite, separating it structurally into two minerals, a hydrated form  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ , and a dehydrated form isomeric with kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Although later work has discredited his structure for the hydrated mineral, the distinction between the two, which often occur together in nature, has been substantiated. Between 1930 and 1937 several workers had noted the presence of mica-like clays in the colloidal fractions derived from shales and soils. These had the main X-ray characteristics of muscovite, but contained less potassium, more magnesium, and more water. In 1937, Grim, Bray and Bradley (7) proposed that a family or group name, illite, be adopted to include such materials which had been variously described as "glimmerton", sericite-like mineral, potash-bearing clay, and hydrous mica. The importance of this group of clays has now been generally recognized, although its detailed mineralogy is still obscure.

The latest group of clays to be identified is of especial structural interest, because, as we shall see later, it can be regarded as forming a link between talc and the montmorillonites on the one hand, and the amphiboles on the other. At the same time, it has a certain close resemblance to the zeolites. These clays, which form the attapulgite-sepiolite group, were described by de Lapparent in 1935, and their structure was elucidated by Bradley in 1940 (4).

Although considerable space has here been devoted to the story of the development of structural formulae for the clays, the contemporaneous advances in the chemistry of the zeolites are also noteworthy. Before the application of X-ray methods, optical and chemical evidence had already made possible a visualization of their general architecture. Their vapor

pressure curves indicated that they could be regarded as porous crystals. The change in optical properties with change in the contents of the pores showed that the latter were regularly arranged, an essential part of the crystal structure. They were known also to have definite pore diameters, since only molecules below a certain size could enter and become absorbed. The X-ray studies, starting with Taylor's structure for analcite (33), disclosed the details of the silicon-oxygen framework, the sites of the exchange cations, and the dimensions of the internal channels. Much of the structural work on the clays was, directly or indirectly, influenced by what had been found for the zeolites. Once structural details of the latter could be envisaged, the way lay open for a detailed reexamination of their absorptive and exchange properties. This was brilliantly accomplished by Hey (11) at the British Museum in the decade from 1929 to 1939. Equally penetrating was Jaeger's structural study of the ultramarine group (14).

Finally, this account of the recent history of the silicate minerals would be completely unbalanced without an appraisal of the contributions from colloid chemistry. Many, perhaps most, of these added new data on colloid-chemical behavior without unfolding new principles. From Wiegner's laboratory in Zürich, however, there came, in the 1920's and 1930's, a stream of papers of decisive import (6, 15, 34, 35, 36, 37). They were illumined by the most acute mind since Liebig's day in that broad field of agricultural chemistry, which, in the inclusive European sense, embraces nutrition and soil science. As if this were not enough, Wiegner added a passionate interest in colloid chemistry, an interest which had first been aroused in the austere laboratory of Zsigmondy at Göttingen, and which he maintained with undimmed enthusiasm to his death.

In broadest outline, the colloid-chemical contributions of the Wiegner school lay in the elucidation of the interactions of charged surfaces with ions in solution. Two main subdivisions of the work are evident to the reader. One was concerned with the mechanism of coagulation, and its relationship to ionic valency and hydration in the intermicellar liquid. The other represented a quantitative continuation of the work of Thomas Way upon base exchange, starting with soils and synthetic permutites and concluding with various natural silicates such as zeolites and certain clay minerals. In this work also the valency and hydration of the cations concerned were seen to be of primary importance. The impact of this work dispelled the idea, widely held by colloid chemists in the early 1920's, that ionic hydration was important only in systems which were themselves extensively hydrated (the so-called emulsoid or hydrophile colloids). It was clearly shown that all negatively charged surfaces, however inert or hydrophobe they might appear, were strongly affected by the hydration of the cation which balanced the negative charge. Comparing cations of equal

valency, a high hydration goes hand in hand with a high *zeta* potential, a relative insensitivity to coagulation, and a ready exchange for ions of smaller hydration. Wiegner well realized that absolute ionic hydration numbers have never been unambiguously determined. He was concerned more with the relative values, employing them in a graphic and qualitative way and visualizing that they might be modified by steric effects when in exceeding close proximity to the molecules of a surface. Actually, as we shall see later, the only established exceptions to his generalizations are caused by such steric effects at anhydrous internal surfaces (the ultramarines). Some apparent exceptions may be traced to fixation, that is, to steric reactions between silicate surfaces and cations of suitable size which operate most markedly on dehydration of the whole system.

In the decade from 1925 to 1935, Mattson's colloid-chemical investigations in the United States exerted a considerable effect upon the thought of the time, especially upon those aspects of silicate chemistry having to do with the formation of soils. He began by studying a considerable range of materials, exploring broadly the colloid-chemical properties of clays from soils, bentonites, mixed hydrous oxides, quartz, and soil organic matter (22). As it progressed, his colloid-chemical work became more and more concentrated upon the mixed hydrous oxides and the gelatinous silicates of indefinite composition, the implicit assumption being that these were the nearest analogs of the actual colloids of soils (23, 24, 25). Conclusions regarding soil formation processes were so closely identified with the properties of these hydrous oxide-silicate mixtures that their correspondence with natural soil colloids seemed to be taken for granted, in spite of the clear evidence to the contrary already provided by Bradfield. Mattson's attitude, notwithstanding his numerous and valuable experiments with clays, finally led to an extreme overemphasis of the hydrous oxide model. It is interesting that Wiegner, however, who for years used the permutites as a model of all base exchange silicates, remained sufficiently detached to recognize, and finally to explore, their limitations. Scientific analogy it would seem, like fire, is a good servant but a bad master.

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## CHAPTER 2

### INTRODUCTION TO SILICATE STRUCTURES

#### *Structural Classification of the Silicates*

The silicate minerals, as the X-ray crystallographers have revealed, possess structures whose geometry is dominated by the disposition of the silicon and oxygen atoms in space. This disposition follows certain well-defined rules, arising in turn from the chemistry and geometry of the atoms themselves. Silicon is a small atom, with a positive electrovalency four and an extremely strong tendency toward a coordination number four. Oxygen is a large atom with a negative electrovalency two and very weak coordination of its own (Fig. 1). Hence, in all the silicates we find a silicon atom esconced in the central pore formed by four oxygen atoms in tetrahedral arrangement<sup>1</sup> (Fig. 2). This unit  $\text{SiO}_4$  has four negative charges. The modern classification of the silicates, due largely to W. L. Bragg and his associates (1) stems from the manner in which these charges are neutralized.

If silicon itself, or some other atom similarly disposed to a tetrahedral arrangement with oxygen neutralizes the charge, then the effect is that the characteristic group  $\text{SiO}_4$  is repeated. This may occur once, or more than once, with each tetrahedral group. If it occurs once we can speak of adjacent tetrahedra sharing a corner oxygen. When it occurs twice then chains or discrete ring structures are produced. When it occurs three times a complete planar sheet results. Finally, when all four oxygens are shared, three-dimensional framework structures appear.

The charges may be neutralized also by a great variety of other cations, acting either independently or in conjunction with repetitions of the  $\text{SiO}_4$  grouping. Their incorporation brings into play important limitations due to their varied sizes, valencies and coordination numbers. It is evident that the completed structure must afford room for the various atoms present, and that all valencies must be satisfied, all charges neutralized. Furthermore, atoms with a strong tendency to certain coordination numbers must find themselves in appropriate positions. The two factors, charge and coordination number, are involved in the important generalization known as Pauling's Rule. This has proved of immense importance in deciding between alternative structures.

<sup>1</sup> If the radius of oxygen is taken as  $1.32 \text{ \AA}$ , then that of the tetrahedral pore surrounded by four oxygen atoms is  $0.30 \text{ \AA}$ , whereas the Si atom has a radius of  $0.39 \text{ \AA}$ . Hence, the oxygens surrounding Si do not quite touch each other.

This rule postulates that charges are balanced by the immediate neighbors. Thus, each cation in any structure is surrounded by a group of anions whose total contribution of negative charge closely balances the positive

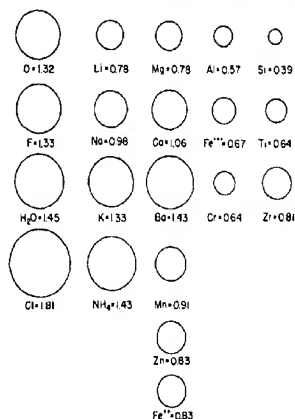


Fig. 1. Relative sizes of the various constituents of the silicates. Numbers given are the radii in Angstrom units ( $= 10^{-8}$  cm.).

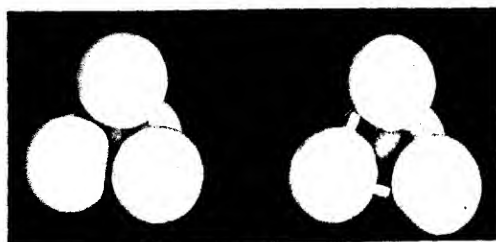


Fig. 2. Silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron. In the latter the larger size of the Al atom causes a widened spacing of the oxygen atoms.

charge of the cation. Simultaneously, the same applies to each anion surrounded by cations.

In the orthosilicates (Olivine,  $(\text{MgFe})_2\text{SiO}_4$ ; Zircon,  $\text{ZrSiO}_4$ ) the whole charge  $(\text{SiO}_4)^{4-}$  is neutralized by cations. We therefore have a salt-like structure. The cations concerned, however, are small compared with oxygen and polyvalent. The electrical attractions are therefore very in-



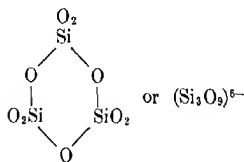
tense, and the structure attained is closely packed. No cases are known in which orthosilicates are so loosely built as to allow for the entry of other atoms. These compounds are for the most part well crystallized and highly insoluble. They can only show colloidal properties in virtue of small particle size, and such occurrences have thus far rarely been found. This may partly be due to the fact that the orthosilicates are only minor constituents of the rocks on the surface of the earth.

In the disilicates (Fig. 3) we find the first evidence of an extremely strong tendency for the charge on the primary  $\text{SiO}_4$  group to be neutralized in part by silicon itself. Two  $\text{SiO}_4$  groups become linked giving  $(\text{O}_3\text{Si-O-SiO}_3)$  or  $(\text{Si}_2\text{O}_7)$  having six negative charges. (The hydrated zinc silicate hemimorphite  $(\text{OH})_2\text{Zn}_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$  belongs to this group.) Compared with the

Fig. 3. Silicon-oxygen grouping in the disilicates,  $(\text{Si}_2\text{O}_7)^{6-}$ , and trisilicates  $(\text{Si}_3\text{O}_9)^{6-}$ , the latter forming a closed ring. (Si atoms not shown).

orthosilicates, the negative charge is smaller and less concentrated. These are also well-crystallized minerals, of somewhat rare occurrence.

The same may be said also of the trisilicates, (Fig. 3) in which a ring forms the basis of the structure (Benitoite,  $\text{Ba Ti Si}_3\text{O}_9$ ).



A larger ring structure containing 6  $\text{SiO}_2$  groups linked by six oxygen atoms is also known (Fig. 4). In the mineral beryl the twelve units of negative charge are neutralized by two aluminum and three beryllium atoms. These are both small and are grouped between adjacent rings. In the center of each ring there is, therefore, considerable free space. The

rings are stacked one above the other giving rise to a system of parallel pores. Beryl, therefore, provides the rare example of a porous structure achieved by the packing of discrete silicate groups. The system of parallel pores, of diameter about 2.5–2.6 Å, should endow it with the capacity to adsorb considerable amounts of gases of small molecular size, such as helium and hydrogen. Water molecules (diameter about 2.9 Å) would be too large for penetration. These conclusions have not as yet been tested by experiment. We could predict also that, since the structure as a whole is electrically neutral, there will be no tendency for small cations to move into the pores and, hence, no capacity for cation exchange. Even if the walls carried a negative charge the lack of interconnections between the pores would

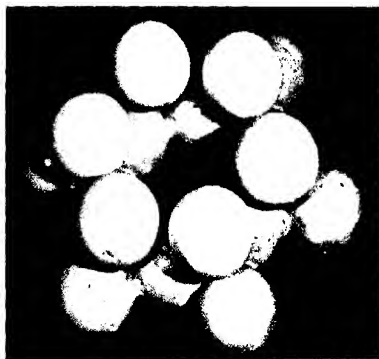


Fig. 4. Ring structure in a hexasilicate  $(\text{Si}_6\text{O}_{18})^{4-}$ , beryl. (Si atoms not shown.)

make exchange reactions exceedingly sluggish, as Hendricks has pointed out (2).

These considerations may now be applied to the second great group of the silicates; those in which silicon-oxygen linkages extend indefinitely in one, two, or three dimensions in space. Here we find practically all the common silicate minerals. Elongated chains of composition  $[(\text{SiO}_3)^{2-}]_n$  are characteristic of the pyroxenes (Fig. 5); double chains of composition  $[(\text{Si}_4\text{O}_{11})^{6-}]_n$  give rise to minerals of the amphibole group (Fig. 6). Sheet structures of composition  $[(\text{Si}_2\text{O}_5)^{2-}]_n$  are typical of the micas and the clays (Fig. 7). Finally, silicon-oxygen linkages extending in all three dimensions give rise to framework structures based on  $(\text{SiO}_2)_n$  of varying degrees of openness. Of these, quartz itself has the closest packing. The feldspars, feldspathoids, ultramarines, and zeolites are progressively more open.

In appreciating these varied structures, certain further peculiarities of the silicates must be borne in mind. In inorganic chemistry it is customary to speak of the isomorphous substitution of one atom for another in a crystal when the two atoms concerned are of comparable size and coordination and of the same valency. Thus, in the group of the alums various trivalent atoms can substitute for aluminum, and various monovalent atoms for

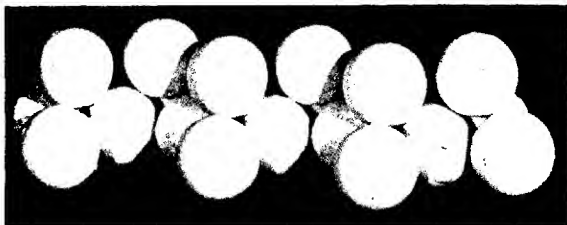


Fig. 5. Single silicon-oxygen chain of indefinite length as in the pyroxenes.  $(\text{SiO}_3)^{2-}_n$ . (Si atoms not shown.)

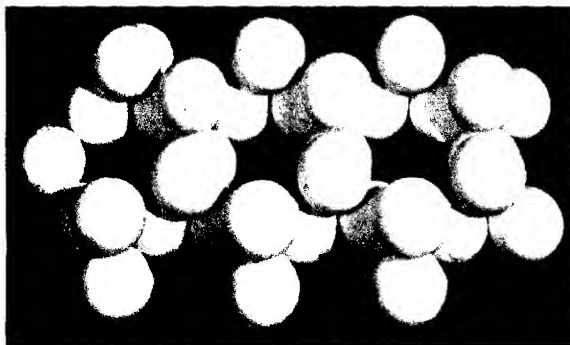


Fig. 6. Double silicon-oxygen chain of indefinite length as in the amphiboles.  $(\text{Si}_4\text{O}_{11})^{6-}_n$ . (Si atoms not shown.)

potassium. In the silicates, however, size and coordination take precedence over valency. Thus aluminum can substitute for silicon at the center of a tetrahedron of oxygen atoms, in spite of the fact that the valencies are three and four, respectively. The tetrahedral group thus acquires a negative charge. This must be neutralized by appropriate cations, for which space must be found in the final structure.

The three-dimensional framework structures (feldspars, feldspathoids, ultramarines, and zeolites) afford clear cut examples of the substitution of  $\text{Al}^{+++}$  cation for Si and of the way in which the nature of this balancing cation is limited by Pauling's Rule. These assemblages of linked tetrahedra afford no positions where six oxygen atoms surrounding an octahedral pore are in contact. Atoms having strong six-fold coordination cannot, therefore, be accommodated. Hence, iron and magnesium are excluded. Spaces surrounded by eight or more oxygens are available. The tendency, therefore, is to incorporate cations such as K, Na, Ca, Sr, Ba, with relatively weak coordination. They readily accommodate themselves with coordination numbers from eight to twelve.

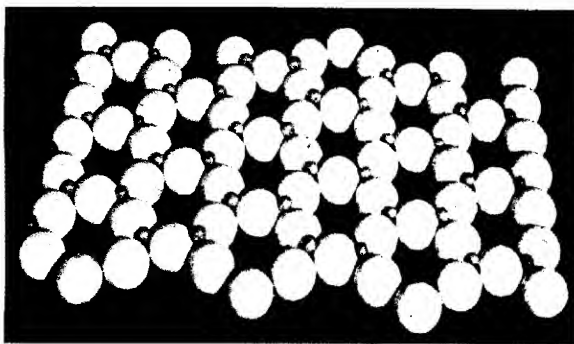


Fig. 7. Silicon-oxygen sheets shown in their commonest hexagonal occurrence with all the silicon atoms on the same side.  $[(\text{Si}_2\text{O}_5)^{2-}]_n$ , as shown without the fourth oxygen and  $[(\text{Si}_2\text{O}_5)^{2-}]_n$  with it.

In contradistinction to the three-dimensional frameworks, the silicates based on silicon-oxygen chains or sheets do contain elements with strong sixfold coordination. The three most important are aluminum, magnesium, and iron. Thus aluminum plays a dual role in silicate chemistry; it can either substitute for silicon in tetrahedral coordination or it can form part of a different unit in which it is coordinated with six oxygens in octahedral arrangement.<sup>2</sup> In the micas and clays, which have silica sheets, the necessary octahedral positions are provided by double sheets of relatively closely packed oxygen atoms. The manner in which these units are combined together will be discussed in detail later.

<sup>2</sup> The octahedral pore, formed of six oxygen atoms in contact would have a radius of 0.55 Å. The Al atom is 0.57 Å in radius and hence causes only a small separation of the oxygen atoms. Magnesium, radius 0.73 Å, causes an appreciable separation.

*Colloidal Properties in Relation to Structure*

1. *Particle Size.* The well-known inverse proportionality between mean particle diameter and specific surface naturally extends over the silicates. If we define the colloidal range as that in which the distinctive reactions of surface molecules become appreciable, then the choice of an upper limit of particle size becomes a matter of the sensitivity of our methods of detection. We are, therefore, precluded from drawing any hard and fast line. In general, however, colloidal properties are well marked in material having one or more dimensions less than  $0.1 \mu$  ( $10^{-8}$  cm.). In the range  $0.1$ – $1 \mu$  they are detectable with varying degrees of difficulty according to the methods employed. Particles larger than  $1 \mu$  are generally regarded as outside the colloidal range, although by highly sensitive methods some of their surface properties can be measured.

Small particle size frequently reflects certain aspects of the mineral structure. A slow rate of crystallization, a very facile cleavage or ready abrasion, all of these are consequences of the atomic arrangement, and all favor the formation, or the subsequent production, of small particles. It is believed also that strains introduced into silicate lattices by the presence of somewhat ill fitting atoms are an important cause of limited growth, and hence favor crystals of colloidal size.

2. *Porous Structure.* Internal pores or channels can naturally increase the specific surface, especially when they are so numerous that all molecular parts of the system become accessible to the outer environment. Such cases have been termed "eugels", and their uptake of neutral molecules "persorption", indicating that here the surfaces and their reactions have reached the ultimate limit. In some instances the solid is amorphous, and the pores assume all sizes, down to the molecular. The silicate water-softeners known as permutites are of this kind. In other cases the pores form an essential part of the crystal structure. They are, therefore, precisely delimited as to size, number, orientation within the crystal, and extent of interconnection. The case of beryl was mentioned above. Other well known examples are the zeolites and ultramarines. Another kind of porous structure is found in the swelling clays, where planar channels of variable width provide access to all lattice units.

3. *Charged Framework.* The properties of silicate surfaces, whether external or internal, depend enormously upon whether ionization can occur by simple dissociation in contact with an ionizing solvent. Such dissociating or polar surfaces arise in two ways. The more important is produced by structures having inherent framework charges. For instance, when Al + K substitutes for Si the potassium atom lies entirely outside the oxygen tetrahedra. In contact with water there is a tendency for the potassium to achieve a certain degree of independence of the silicon-oxygen framework. The extent will depend upon the properties of the solvent, those of the

cation, the distribution of charges in the framework, and the dimensions of the pores. This may be contrasted with the case of an anhydrous silica skeleton alone, in which there is no substitution, a completely neutral silicon-oxygen framework, and no mechanism for ionization. In each case we can envisage an extensive and accessible surface. The two will differ least in respect to properties which do not involve ionization or the orientation of dipoles. For instance, the adsorption of inert gases at low temperatures might be fairly comparable for equal specific surfaces. On the other hand, the behavior toward water and the electrochemical properties of the solid-liquid systems would be entirely different.

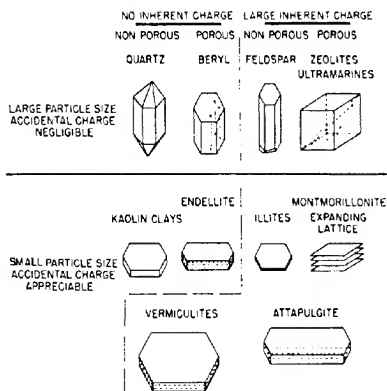


Fig. 8. The factors particle size, inherent charge, and porosity as they determine the colloidal properties singly or in combination.

(Note that vermiculites occur in large and small particle sizes.)

A second mechanism for production of a charged surface is accidental rather than inherent. In the termination of a lattice the valency relationships of the constituent atoms are sometimes "upset". We may speak of unsatisfied or free valencies, or of broken bonds, which, of course, do not remain so, but, by reaction with a solvent, produce local ionization. The number of these accidental charges depends on the degree and nature of the subdivision. This comes to light very clearly in the clay mineral kaolinite. The flat cleavage surfaces of this platy mineral are believed to be chemically inert, having no inherent or accidental charges. They do not contribute to ionization. The edges of the cleavage flakes, however, do contain broken bonds, which by reaction with ionizing solvents produce localized charges. Thus, the electrochemistry of kaolinite is chiefly the electrochemistry of its exposed edges.

In most colloidal silicates two or more of the above factors contribute to the ensemble of the colloidal properties (Fig. 8). Thus, as we shall see later, the zeolites and ultramarines combine a porous structure with a high inherent framework charge. The clay mineral attapulgite has a moderately small particle size, a porous structure, and both inherent and accidental charges. Kaolinite has small particle size and an accidental charge. Beryl has a high porosity toward small molecules only, but no appreciable framework charge; and since the particle size is usually large, accidental ionization plays no measurable part. The clays of the montmorillonite group combine all four of the above factors, but their great porosity and high inherent charge dominate the situation. The compact clays of the hydrous mica group have no internal porosity but their inherent charge is high. This, combined with the accidental charge due to small particle size gives the clue to their colloidal properties.

#### *Silicates and the Processes of Solution*

Since we shall be greatly concerned with ionization and the effects of water molecules on colloidal silicates it is well to consider the restricted meaning of the term 'solubility' as applied to silicates generally. Even the orthosilicates, disilicates, *etc.*, with their discrete groups, differ materially from sparingly soluble salts like barium sulphate. No well-defined silicate ions are found, even in cases where small quantities of material pass into solution. It is generally assumed that, because silicic acid is so weak, hydrolysis plays an important part. Once the silicic acid is released its strong polymerization tendency operates and further complicates the situation.

In those silicates having indefinitely extending structures, with which we shall chiefly be concerned, the whole concept of solubility loses its precise meaning. Material released from the framework consists of fragments only. They bear no relation to the unit cell, which is a purely geometrical concept. Furthermore, since points of weakness in the silicon-oxygen framework (caused, for instance, by substitution of Al for Si) are distributed at random, the fragments released are not uniform in size or in composition. This is seen very clearly when an electric field is applied to a silicate under mild attack by hydrogen ions. Fragments containing silicon frequently are found migrating both to the anode and the cathode chambers. Some are, therefore, positively charged, others negatively, depending upon the accidental balance of charges at the instant of release.

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## CHAPTER 3

### SILICATES BASED ON A THREE-DIMENSIONAL FRAMEWORK

The three-dimensional frameworks are all characterized chemically by two interdependent descriptions; the ratio  $O:Al + Si = 2.000$ , and mono plus divalent bases (in equivalents) = Al atoms. In addition, for individual members, the charge on the framework must be defined either by  $Al/Al + Si$  or, what amounts to the same thing, by mono plus divalent bases (in equivalents)/ $Al + Si$ . Our knowledge of the detailed geometry of this whole group is by no means complete; indeed, for the feldspathoids it is almost entirely by inference and analogy rather than by direct demonstration. We are reasonably well-informed regarding the feldspars, the ultramarines, and some of the species of zeolites.

#### *The Feldspars and Feldspathoids*

In Table I the chemical compositions are given with reference to some simple fraction of the unit cell as determined by X-ray measurements. In the feldspars it is one-quarter, in the feldspathoids one-eighth. The main features of the feldspar structure as outlined by Bragg (1) may be seen in Fig. 9. Since the silicon and aluminum atoms are small and are accommodated in the tetrahedral pores between four oxygen atoms (*albeit with some distortion in the case of Al*) they are not shown. The white balls, representing oxygen, are seen to form complex chains, two of which are visible. These are crosslinked at intervals, and in the intervening spaces potassium atoms, represented by black balls, are accommodated. This is the essential structure of orthoclase. Albite differs from it in the substitution of Na for K and by a slight readjustment of the framework to the smaller size of the sodium atom. Anorthite is similar to albite, except that calcium takes the place of sodium, and the extent of substitution of Al for Si is consequently doubled.

The environment of the potassium, sodium or calcium consists of oxygen atoms, six of which are relatively close and four at a somewhat greater distance. If we take the atomic radii given by Bragg (1) for these atoms we see that the potassium (radius  $1.33 \text{ \AA}$ ) in orthoclase, at  $2.85 \text{ \AA}$  (center to center) from the nearest oxygen atoms, actually only has  $0.1 \text{ \AA}$  free space surrounding it. Thus, there is no possibility of external solutions acting upon the structure except by the successive replacement of potassium atoms by hydrogen starting from the external surface. In this way, a space approxi-



mately large enough to accommodate a single water molecule (radius 1.38–1.45 Å) is made available. Thus, the decomposition of the feldspars only becomes possible as the potassium, calcium or sodium is removed and the

TABLE I  
*Compositions of Feldspars and Feldspathoids*

Group	Name	Composition	Framework Charge Ratio Al/(Al + Si)
Feldspar	Orthoclase	$K \cdot AlSi_3O_8$	0.250
"	Microcline	$K \cdot AlSi_3O_8$	0.250
"	Anorthoclase	$(Na, K)AlSi_3O_8$	0.250
"	Celsian	$Ba \cdot Al_2Si_2O_8$	0.500
"	Albite	$NaAlSi_3O_8$	0.250
"	(Intermediate plagioclase members)		0.250–0.500
"	Anorthite	$CaAl_2Si_2O_8$	0.500
Feldspathoid	Leucite	$KAlSi_2O_6$	0.333
"	Nepheline	$NaAlSiO_4$	0.500
"	Kaliophilite	$KAlSiO_4$	0.500



Fig. 9. Model of orthoclase, showing the situation of potassium (black spheres) in relation to the silicon-aluminum-oxygen framework. (The Si and Al are not shown.)

structure becomes permeable, albeit sluggishly, to water molecules. The evidence on decomposition adduced by Tamm (6) shows that complete breakdown of the original structure follows the primary replacement of the

cation by hydrogen. In the case of microcline, at pH values around 6 it appeared that reversible interchange of potassium and hydrogen was possible, but with oligoclase (Na-Ca plagioclase) irreversible changes operated throughout.

Thus, it is doubtful whether one can speak strictly of the colloid chemistry of the feldspars, but rather of the colloid chemistry of their decomposition. Tamm's colloidal suspensions of decomposing feldspar, produced on grinding in the presence of water or benzene, are thus essentially unstable. In the finest fractions of naturally occurring clay ( $<0.1 \mu$ ), feldspar has only recently (3) been positively identified and it has rarely been found in the total clay fraction as defined by soil scientists ( $<2 \mu$ ). The unweathered glacial clays, produced and deposited under low temperature conditions in Scandinavia, and in Canada, do contain feldspar in the  $2 \mu$ - $0.1 \mu$  range and are exceptional (3, 6). The colloid chemistry of the decomposition processes and products is of great importance to geochemistry, but the whole field of study is practically virgin. Mattson's work (5) on the conditions for the isoelectric precipitation of hydrated silica-alumina gels is relevant in part. There is also considerable mineralogical information on high temperature decomposition of the feldspars in presence of water or aqueous solutions. How far this may be applied to low temperature conditions is not known.

The structures of the feldspathoids are at present incompletely known, but they apparently possess a three-dimensional framework with a higher replacement of  $K + Al$  or  $Na + Al$  for  $Si$  than the corresponding feldspars. They decompose more readily than the latter in presence of aqueous solutions. Thus leucite,  $KAlSi_3O_8$ , can be converted into analcite,  $NaAlSi_3O_8 \cdot H_2O$ , a zeolite, by heating with concentrated solutions of sodium salts. It is not certain whether the greater ease of decomposition of the feldspathoids as compared with the feldspars is due to their higher lattice charge or to a slightly more open structure.

#### *The Ultramarine Group*

Besides lazurite and the synthetic ultramarines of similar composition several other minerals may be included in the group. They are all cubic, having similar structures characterized by the presence of both anions and cations as mobile constituents within the pores of the negatively charged framework. The scapolite group of minerals has somewhat similar properties, but the tetragonal structure is quite different from that of the cubic ultramarines. The compositions of the most important members are listed in Table II.

As an illustration of these structures, Fig. 10, redrawn from Jaeger's monograph (4), gives the essential features of ultramarine. The mobile anion group is not shown, but it resides in the large central pore. This is

connected to other similar pores by channels containing the mobile Na atoms. We should, therefore, expect to find ready exchange both of anions and cations. The large anions, however, are less easily replaced than the cations, fusion with salts being needed, whereas the cations can be replaced from hot aqueous solutions. Jaeger has shown that silver readily replaces sodium and has then carried out quantitative experiments on the replacement of silver by other ions. He states: "Under equal conditions of temperature, concentration, and duration of heating, the silver is replaced more rapidly and completely as the atomic weight of the alkali metal decreases. Replacement is most rapid and complete with lithium, followed in decreasing order by Na, K, Rb, and Cs. Ammonium ( $\text{NH}_4$ ) is about equivalent to K in its action." In this anhydrous structure, therefore, the small ions enter more readily than the larger. As will be pointed out later, this is the converse of the usual base exchange order for hydrated systems.

TABLE II  
*Compositions of Ultramarines*

Group	Name	Composition	Framework charge ratio $\text{Al}/(\text{Al} + \text{Si})$
Sodalite	Sodalite	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{Cl}_2$	0.500
	Noselite	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{SO}_4$	0.500
	Häüynite	$(\text{Na}, \text{Cs})_{1-2}\text{Al}_6\text{Si}_6\text{O}_{24} \cdot (\text{SO}_4)_{1-2}$	0.500
Helvite	Helvite	$(\text{Mn}, \text{Fe})_2\text{Be}_2\text{Si}_6\text{O}_{24} \cdot \text{S}_2$	0.667
	Danalite	$(\text{Mn}, \text{Fe}, \text{Zn})_2\text{Be}_2\text{Si}_6\text{O}_{24} \cdot \text{S}_2$	0.667
	Lazurite	$\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{S}_4$	0.500
Ultramarine	Synthetic	$\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{S}_4$	0.333
	(high Si)		
Scapolite	Marialite	$\text{Na}_4\text{Al}_3\text{Si}_7\text{O}_{24}\text{Cl}$	0.250
	Meionite	$\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4, \text{CO}_3)$	0.500

Jaeger mentions that the synthetic ultramarines produced by fusion consist of very small crystal units in aggregate form. When these are ground with water, the resulting paste has some plastic and hydraulic properties which apparently have never been fully investigated. Their study from the colloid chemical viewpoint should prove worthwhile.

#### *The Zeolites*

The structural chemistry of the zeolites has been enormously advanced in the past twenty years by the close collaboration of W. L. Bragg's school of X-ray crystallographers with mineralogists of the British Museum. The chemical compositions of a number of these minerals, whose structures are fairly clearly established, are listed in Table III.

Like the feldspars, feldspathoids, and ultramarines, these are three-dimensional structures in which replacements of  $\text{Al}^+$  cation for Si

operate to a variable extent. They differ from the above groups in being hydrated. No mobile anions are present. The zeolites are characterized by a reversible dehydration reaction in which the essential framework remains unchanged (except that in certain cases lattice shrinkage occurs at high temperatures). They also show cation exchange in contact with aqueous solutions of salts. The speed of this reaction varies enormously in different cases.

TABLE III  
Composition of Zeolites

Group	Name	Composition	Framework charge ratio Al/(Al+Si)
Fibrous	Natrolite	$\text{Na}_4\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 4\text{H}_2\text{O}$	0.400
	Mesolite (approx.)	$\text{Na}_{1-1.5}\text{Ca}_{1.5}\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 5\frac{1}{2}\text{H}_2\text{O}$	0.400
	Seolcite	$\text{Ca}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 6\text{H}_2\text{O}$	0.400
	Edingtonite	$\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 8\text{H}_2\text{O}$	0.400
	Thomsonite	$\text{NaCa}_2\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 6\text{H}_2\text{O}$	0.500
Heulandite (platy)	Heulandite	$\text{CaNaAl}_3\text{Si}_3\text{O}_{14} \cdot 12\text{H}_2\text{O}$	0.167
		$\text{Ca}_2\text{NaAl}_3\text{Si}_3\text{O}_{14} \cdot 12\text{H}_2\text{O}$	0.278
Cubic	Analcite	$\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$	0.333
	Chabazite (approx.)	$(\text{Ca}, \text{Na}_2)_2\text{Al}_4\text{Si}_3\text{O}_{21} \cdot 12\text{H}_2\text{O}$	0.333
	Gmelinite	$\text{Na}_4\text{Al}_4\text{Si}_4\text{O}_{24} \cdot 12\text{H}_2\text{O}$	0.333

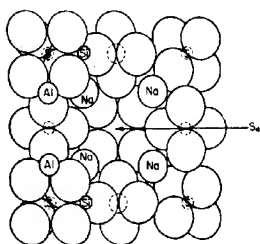


Fig. 10

Fig. 10. Structure of ultramarine according to Jaeger.

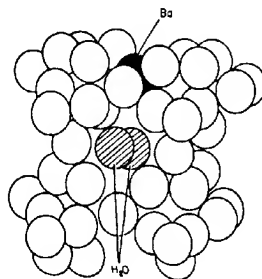


Fig. 11

Fig. 11. Structure of the fibrous barium zeolite edingtonite.

Fig. 11 illustrates the structure of the barium zeolite edingtonite. (The small silicon and aluminum atoms are omitted.) The structure is very open, with ample room for movement of water molecules and barium ions. This structure, with but slight modification, characterizes all the zeolites listed in the fibrous group. It consists of chains of linked tetrahedra (extending vertically in the figure) joined together at intervals to give a three-dimensional framework (9).

Heulandite, which cleaves very readily into thin plates, probably consists of strong, indefinitely extending silicon-aluminum-oxygen sheets, linked in a vertical direction to form layers of limited thickness (7). These are then presumably linked together by cations and water molecules. In harmony with this somewhat incompletely determined structure is the fact that on dehydration a 10% shrinkage occurs at right angles to the plane of the sheets. If the suggested structure is correct, heulandite contains sheets of water molecules and exchangeable cations, a situation which we shall encounter again in the swelling clays.

The structure of the cubic zeolite analcite has been very fully worked out by Taylor (8). The three-dimensional framework is constructed in such a way that channels containing water molecules lie along the three-fold axes, that is, along the cube diagonals. The sodium ions fill only two-thirds of the equivalent positions available and presumably can wander into vacant positions, thus achieving a statistically randomized arrangement.

Less is known of the detailed structure of chabazite, but Wyart (10) suggests that it is closely analogous to that of sodalite in the ultramarine group. Both are cubic minerals. The calcium ions are placed in wide channels along the three-fold axes. The exact distribution of the water molecules is not determined. The structure is probably somewhat more open than that of analcite, since chabazite contains the highest proportion of water of any of the zeolites, and it enters into base exchange equilibria with great facility.

#### *Structural Factors of Importance to the Colloidal Properties*

In classifying and discussing the silicate minerals, there is a natural tendency to regard the framework as the most important unit, with cations, small anions, and water molecules as accessories. It is probable, as Taylor points out (7), that this approach is over-simplified, and that even the most mobile constituents have some influence upon the framework structure at the moment of synthesis. Even when crystallization has been completed, replacement of one cation by another of comparable size frequently leads to framework readjustments. It appears as though the cations and the water molecules orient themselves with respect to the framework and to one another in certain preferred arrangements. However, since it has not proved possible to distinguish between Si and Al in the framework by X-ray methods, the exact relation between the seat of the negative charge and the cation position is not known. Pauling's principle, which implies that the charges are balanced over the shortest possible distances, affords some general guidance. It has frequently been used in deciding between alternative structures.

The cations, as is general in inorganic chemistry, show a tendency to

assume certain coordination numbers, by taking up positions where they are surrounded by oxygen atoms of the framework, or, in the zeolites, by water molecules also. In the minerals considered above, this tendency, due to the nature of the cations concerned, (Na, K, Ca, Ba) is relatively weak. These ions are found, with six, seven, eight, or even ten, near neighbors, often unequally spaced. In a few extreme cases the attempt to replace one of these ions with others of the same valency but different coordination properties leads to disruption or rearrangement of the whole structure. Generally, however, ions of the same valency and appropriate sizes can

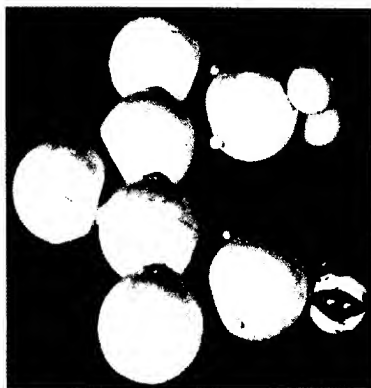


Fig. 12. Disposition of water molecules in the zeolites according to Taylor (7). The exposed oxygen atoms of the silicate framework are on the left. The upper right shows the tetrahedral arrangement in which a water molecule has two hydrogens (small beads) bonded to the framework oxygen and to two cations (sodium, large beads). In the lower right we have a similarly situated water molecule coordinated with one divalent cation (calcium, large striped bead).

replace each other without alteration of the framework. Readjustments of the number of water molecules present frequently accompany such changes. Taylor has shown that in most cases the water molecule can be represented as taking up a special configuration between the cation and the oxygen of the framework. The hydrogen atoms can be regarded as directed toward two framework oxygens, while the oxygen atom of the water lies close to a divalent cation or equidistant from two monovalent cations. Thus, the water molecule has in effect four partial valencies tetrahedrally arranged (Fig. 12). Evidence for this view is shown by natrolite, in which sodium can be replaced by ammonium. The ammonium natrolite, however, is anhy-

drous, thus  $\text{NH}_4^+$  has replaced  $\text{Na}^+ \cdot \text{H}_2\text{O}$ . Taylor suggests that the  $\text{NH}_4^+$  ion, because of the tetrahedral structure, can substitute for the water and, at the same time, can balance the negative charge on the framework. Other less extreme cases are found among the fibrous zeolites. Scolecite, the fibrous calcium zeolite with  $6\text{H}_2\text{O}$ , was shown by Hey (2) to give natrolite and lithium natrolite, respectively, each with  $4\text{H}_2\text{O}$ , when fused with sodium chlorate or with lithium nitrate. Here, four monovalent ions have replaced two divalent ions plus two water molecules.

The presence of unfilled lattice positions is regarded by Bragg as especially important in facilitating base exchange. In the feldspars all positions are occupied; thus, interchange of the type  $\text{Ca}^{++} \rightleftharpoons 2\text{Na}^+$  is impossible. The zeolites, however, contain numerous vacant positions, both with respect to the cations and to the water molecules. Interchange can thus occur with ions of different valencies, although in some cases, notably that of thomsonite, it is exceedingly sluggish and apparently limited in extent.

The sizes, number and disposition of the channels provided by the framework will also be of great importance in determining the speed of ionic exchange and of hydration reactions. An upper limit of ionic or molecular size, beyond which no entry is possible, will be set by the largest channels present. In most of the structures considered, these are not discrete, but either intersect or are joined by an interpenetrating system of smaller channels. In the fibrous zeolites, for instance, it is supposed that the water molecules lie in the larger channels parallel to the *C* axis, while the cations are accommodated in the smaller connecting channels. The close connection between water molecules and cations is, however, maintained.

From Tables I-III it will be seen that, when Al replaces Si, the maximum framework charge ratio is 0.500; that is, not more than half the silicon is substituted by aluminum. Beryllium, also, does not replace silicon to a greater extent than one-half, but, because of its divalent character, framework charge ratios greater than 0.500 are possible. As we shall see later, the framework charge ratio is important in determining how far decomposition can proceed without complete disruption of the framework. It evaluates the main electrostatic property of the framework skeleton, that is, its capacity for attracting cations.

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## CHAPTER 4

### THE COLLOIDAL PROPERTIES OF THE ZEOLITES

#### *The Adsorption of Gases and Vapors*

A considerable volume of earlier work on the adsorption of gases and vapors by crystalline zeolites has been reviewed by McBain (22) and by Hey (13) so that here we need only take up those aspects relating to structure. Interest centered from the first around the nature of the dehydration curves, which do not form steps like true hydrates but give smooth continuous curves. Tammann showed later that the same was true of the isotherms. The analogy with adsorption on materials such as charcoal, artificial permutites, and silica gel seemed exceedingly close. In one respect, however, the zeolites differed from the other adsorbents. They took up only small molecules, as was most strikingly shown for chabazite by Weigel and Steinhoff in 1925 (31). It appeared, therefore, from the chemical evidence alone, that the pores were limited in size and exceedingly numerous. The term "persorption" was introduced by McBain to explain the uptake of gases and vapors as being due to the progressive filling of these molecular-sized pores.

As regards the phase rule, the system zeolite-water can be treated as a solid solution of a hydrate in the anhydrous phase. This approach (due to Tammann) is favored by Hey (13). It has the advantage that irreversible effects can be readily explained as being due to lattice shrinkage or other rearrangement. It has, further, the support of much of the modern X-ray work, which has shown that in many cases there is incomplete filling of the pores with water molecules, even under conditions approaching saturation. In some cases also, the water molecules fall into distinct sets, thus approaching the case where well-defined hydrates can coexist. It is characteristic of the zeolites that each set shows a continuous dehydration curve. The existence of several sets makes itself apparent by smooth changes in curvature, not by sharp breaks.

The theory of Hey (14) provides a means of comparing the sorption properties of the zeolites with respect to different gases and vapors. In order to make use of it, both isobaric and isothermal data are required. Hey has furnished such data by determining isohydric curves (that is, curves connecting vapor pressure with temperature at constant composition) for various compositions, supplemented, in certain cases, by isobaric dehydration curves. In this way the composition-vapor pressure-temperature surfaces have been drawn for the following zeolites; thomsonite

and metathomsonite (15), natrolite (16), mesolite (17), edingtonite (18), scolecite, and metascolecite (19). In addition, he has recalculated the data of Friedel on analcite (10) and chabazite (11), and that of Tiselius and Brohult (27) on chabazite. In all the above cases, water vapor formed the gaseous phase. The theory has also been applied to the systems chabazite-nitrogen and chabazite-hydrogen using Rabinovitch's data (24).

The original (14) should be consulted for a discussion of the assumptions and uncertainties involved, but Fig. 13 will help to clarify the salient points. Sorbed molecules of effective radius  $\rho$  are spaced at equal intervals  $D$  along pores of effective radius  $r$ . For a molecule to enter the pores, it must strike within an area  $a = \pi(r - \rho)^2$ . Further, in order to condense, its kinetic energy must exceed a certain activation energy  $\eta$ . To escape, an activation energy of evaporation  $\epsilon$  must be exceeded. The energy difference per gram-molecule is then  $E = N(\epsilon - \eta)$  where  $N$  is Avogadro's number

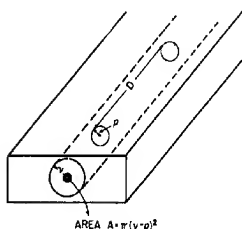


Fig. 13. Hey's theory illustrated by a single pore.

For changes of composition centering around the fraction  $x$ , which represents the fraction of sites for absorption actually occupied, the following equation is derived:

$$\log p = C + \frac{1}{2} \log T - \log \frac{x}{1-x} - E \frac{(\log e)}{RT}$$

where  $C = 5.22 + \log \frac{\sqrt{E}}{aD\chi}$ ,  $p$  is the vapor pressure at equilibrium and  $\chi$  is a factor involved in calculating the time of escape of the gaseous molecule. It is taken as 1 in the computations.  $E$  is related to the heat of absorption  $Q_s$  by  $Q_s = E + \frac{1}{2}RT$ . The above equation only applies where  $E$  is independent of  $x$ . This is frequently not the case. However, a linear relation between  $E$  and  $x$  is usually found, so that a slightly more complex equation can be used. This means that, as water is removed, the remainder is more firmly bound. In some cases,  $C$  also shows a variation with  $x$  not

accounted for by variation in  $E$ . This is due to lattice shrinkage, a small amount of which can cause a large diminution in  $a$ , the effective area of condensation. In using this equation, it is assumed that the volatile molecules considered form only one set. In cases where two or more sets show little interference, each can be dealt with separately.

From the experimental results, combined with values of  $D$  obtained from X-ray data, the area of condensation  $a$  can be calculated. Using the accepted value, 1.45 Å, as the effective radius of the water molecule, Hey has calculated the channel radius in a number of cases: edingtonite 1.52 Å, mesolite 1.48 Å, natrolite 1.50 Å at full hydration and 1.46 Å dehydrated, chabazite 1.46 Å from Friedel's data and 1.49 Å from Tiselius and Brohult's data, analcite 1.71 Å. Thus, the water molecules have little free space by which to enter, except in the case of analcite. The data for chabazite-nitrogen and chabazite-hydrogen were handled somewhat differently. Using 1.49 Å as the channel radius, the molecular radii for the two gases were calculated, and were found to be in good agreement with accepted values.

Since the variation in  $Q_z$ , the heat of hydration, with temperature is small, the isohydric curves when plotted as  $\log p$  against  $1/T$  give practically straight lines, in agreement with experiment. The results can be used to give  $Q_z$ , the heat of hydration. Table IV summarizes these values. To make more precise comparisons between the different zeolites, the number of molecules sorbed has been recalculated to a uniform basis of 80 framework oxygen atoms. This corresponds to the unit cell of some of the fibrous zeolites.

It is evident in these structures that a relatively high degree of hydration per framework unit of 80 oxygen atoms is not always accompanied by a low heat of hydration. Taking each mineral separately, however, the heat of hydration rises as dehydration proceeds, but not uniformly as a rule. In the case of natrolite, pronounced lattice shrinkage accompanies the dehydration at higher temperatures. In edingtonite the water molecules form two distinct groups, while scolecite shows a transition to metascolecite, a change accompanied by marked shrinkage. These complexities can only be fully appreciated from the original papers, but their influence is readily shown by the isobaric dehydration curves for 10 mm. pressure. These are reproduced in Fig. 14. Chabazite gives a simple curve since the water molecules belong to one set only. Edingtonite has two sets, the curves showing corresponding changes of slope. Natrolite shows the effect of a pronounced lattice shrinkage.

Comparatively little work has been done on the vapor pressure relationships of zeolites which have undergone base exchange. Löwenstein (21) found that the vapor pressures of potassium and ammonium chabazites

and stilbites at room temperature were higher than those of the two calcium zeolites. Similarly, potassium heulandite had a higher vapor pressure than calcium heulandite. At fixed vapor pressures, the potassium and am-

TABLE IV  
*Thermochemical Data on the Sorption of Gases and Vapors by Zeolites*

Author and reference	Zeolite	Molecule sorbed	Range in molecules per 80 oxygen atoms of framework	Heats of sorption cal./g. molecule
Hey (15)	Thomsonite	H <sub>2</sub> O	23.8-7.7	15,900-71,600
" (15)	Metathomsonite	H <sub>2</sub> O	19.5-7.7	13,700-18,400
" (16)	Natrolite	H <sub>2</sub> O	16.0-0.8	7,050-25,850
" (17)	Mesolite	H <sub>2</sub> O	21.3-2.3	10,500-32,800
" (19)	Scolecite	H <sub>2</sub> O	24.0-8.0	22,400
" (18)	Edingtonite	H <sub>2</sub> O	32.0-9.6	10,800-25,900
" (14)	Analcite	H <sub>2</sub> O	13.3-0.0	18,300
" (14)	Chabazite	H <sub>2</sub> O	40 -12	15,100-18,500
Tiselius (29)	Heulandite	H <sub>2</sub> O	27 -17	12,500-17,590
" (29)	Analcite	NH <sub>3</sub>	0 -13.3	16,000
" (20)	Chabazite	NH <sub>3</sub>	2.4-3.6	16,500
" (28)	Chabazite	CO <sub>2</sub>	7.2-15.5	7,750- 4,920
Rabinovitch (24)	Chabazite	N <sub>2</sub>	0 -17.8	5,000- 2,000
" (24)	Chabazite	H <sub>2</sub>	~0	1,800
Barrer (1)	Chabazite	H <sub>2</sub>		4,000- 1,700
" (1)	Analcite	H <sub>2</sub>		1,500- 1,400
" (1)	Analcite	He		500
" (1)	Chabazite	A		6,000- 2,900
" (1)	Analcite	A		3,700- 3,300
" (1)	Chabazite	N <sub>2</sub>		8,800- 4,400
" (1)	Analcite	N <sub>2</sub>		5,500- 5,000
" (1)	Chabazite	NH <sub>3</sub>		28,600-22,700
" (1)	Analcite	NH <sub>3</sub>		22,700-14,200
" (1)	Natrolite	NH <sub>3</sub>		{ 15,050- 8,040 (surface) 11,830- 10,050 (interior)
" (5)	Chabazite	CH <sub>4</sub>	(15% saturation)	4,700
" (5)	Analcite	CH <sub>4</sub>	"	3,800
" (5)	Chabazite	C <sub>2</sub> H <sub>6</sub>	"	8,150
" (5)	Analcite	C <sub>2</sub> H <sub>6</sub>	"	7,400
" (5)	Chabazite	C <sub>3</sub> H <sub>8</sub>	"	9,750
" (5)	Chabazite	n-C <sub>4</sub> H <sub>10</sub>	"	11,150
" (5)	Analcite	n-C <sub>4</sub> H <sub>10</sub>	"	9,300

monium compounds had lower moisture contents than the corresponding calcium compounds.

Hey (17) found that, at 110°C. and 1-3 mm. pressure of water vapor,

mesolite (Ca-Na) contained more water than natrolite (Na). The lithium compound was more hydrous than the sodium compound. The potassium mesolite was less hydrous and the ammonium natrolite was completely anhydrous at this temperature.

The sorption of gases and vapors other than water has been studied chiefly with chabazite (see McBain's review); heulandite, analcite, thomsonite, and mordenite have also been used. It is found, in agreement with structural studies, that molecules below a certain size are taken up readily by dehydrated zeolites. The quantities sorbed depend on the relation between the temperature of observation and the critical temperature of the gas or vapor concerned, also on the polar character of these molecules. The heats of sorption increase very strikingly as the polar character be-

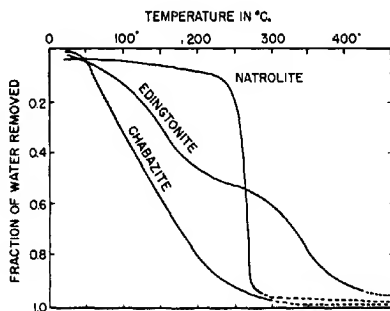


Fig. 14. Isobaric dehydration curves at 10 mm. pressure of water vapor for edingtonite, chabazite, and natrolite. (Hey)

comes more pronounced. Hey (15) has suggested that the distribution of foci of residual affinity along the lattice pores has a strong influence on the sorption of alcohols by thomsonite. If the hydrocarbon chains are of such length that OH groups can accommodate themselves to the centers of residual affinity, then uptake is facilitated, provided the molecule is suitable in other respects. Ethyl alcohol, isopropyl alcohol, and ethylene glycol were all strongly taken up, while *n*-propyl and the three butyl alcohols were not.

Chabazite readily takes up gaseous molecules smaller than that of ethyl alcohol. Propylene and ethane are on the borderline, but ethylene is strongly sorbed, and so are methyl alcohol, methylamine, and formic acid. Tiselius (28) has made the important observation that the absorption spectrum of dehydrated copper chabazite changes to that of cuprammonium

compounds when ammonia gas is sorbed. This means that the copper atoms are coordinated with ammonia within the crystal and, by analogy, lends support to Taylor's idea that the water molecules in zeolites are definitely coordinated with the cations.

As compared with chabazite, heulandite is less reactive (29). It readily takes up ammonia or water but carbon dioxide and ethylene are sorbed only slightly. The water molecules probably form several sets. Analcite is less reactive than heulandite and, even with ammonia, equilibrium is quickly attained only at high temperatures.

The systematic study of the sorption of molecules of varying sizes has been considerably advanced by Barrer (1-7). His thermochemical data are given in Tables IV and V. Helium has an extremely low heat of sorption; nevertheless, at low temperatures, dehydrated chabazite takes up helium approximately equivalent to the water previously lost. This is true also for argon, whereas only about half the equivalent quantity of nitrogen is sorbed. In the hydrocarbons there is a pronounced increase in the heat of sorption with increase in chain length. Strongly polar small molecules, like ammonia and water, show much greater heats of sorption than do relatively inert molecules. For the particular cases studied by him Barrer has arranged the zeolites into three classes, as follows:

Class I. Chabazite, gmelinite, active analcite. Ethane, methane, and smaller molecules are readily occluded, *n*-propane is occluded slowly. Iso-paraffins are completely excluded.

Class II. Mordeite (natural Ca, K, Na zeolite). All paraffins excluded except ethane and methane which are slowly occluded. Nitrogen and similar gases occluded.

Class III. Calcium and barium mordenites prepared by base exchange at higher temperatures. Negligible occlusion of all paraffins. Nitrogen and similar gases occluded.

The most interesting structural aspect of these results lies in the change in the sorptive properties of mordenite when calcium or barium is substituted for sodium and potassium. X-ray data indicated that a slight lattice shrinkage accompanied the exchange, thus reducing still further the pore diameter. Ethane and methane then can no longer enter, and nitrogen becomes the largest molecule occluded.

#### *Rates of Diffusion*

Hey (14) has extended the theory of gas-zeolite equilibria to account for rates of diffusion into the crystalline solid. To do this, he has postulated an activation energy  $\mu$  for migration within the lattice. The theory has been tested by utilizing the data of Tiselius for the water-heulandite and am-

monia-analcite systems. The activation energies for migration were calculated from the temperature coefficients of the rates of diffusion. Using an elegant optical method, Tiselius (28) had shown that two different rates of diffusion existed for directions normal to the faces (201) and (001). Hence, two activation energies for migration were calculated as follows:

$$(N\mu)_{201} = 5400 \text{ cal./g.-mol.}$$

$$(N\mu)_{001} = 9140 \text{ cal./g.-mol.}$$

These values are considerably lower than the activation energies for absorption (about 14,100 cal.) given in Table IV. For the ammonia-analcite system, the activation energy for migration was calculated to be 13,500 cal./g.-mol., whereas for the sorption process it was about 16,000 cal./g.-mol. It would seem, therefore, that within the water-heulandite

TABLE V  
*Apparent Energies of Activation ( $E_A$ ) for Diffusion of Solutes within Lattices of Various Zeolites*

(Barrer and Ibbitson, 3)		
Zeolite	Molecule	$E_A$ (cal./g.-mol.)
Chabazite	Propane	4,500, 6,700
"	n-Butane	8,900, 8,600
"	n-Pentane	7,100, 6,800
"	n-Heptane	11,000, 11,400, 9,800
"	Ethyl formate	7,300
"	Methyl acetate	4,000
"	Propionitrile	5,900
Analcite (active)	Propane	6,800, 7,300
Mordenite	Ethane	4,300
"	Acetonitrile	8,300
Ba-mordenite	H <sub>2</sub>	3,500
"	A	4,900
Ca-mordenite	H <sub>2</sub>	1,040

system water molecules can move relatively freely as compared with ammonia molecules in analcite. However, in heulandite the water is held in several sets with different energies of absorption and different diffusion constants and a full comparison at all stages of dehydration is not yet possible.

Barrer and Ibbitson have calculated apparent energies of activation for diffusion from place to place within the lattice (Table V). They believe that molecules with cross sectional diameters less than 4.0 Å are taken up by a process resembling free diffusion down very minute channels. For larger molecules which can still enter the channels, there is a much slower process in which an energy of activation is needed to move the molecule along from one position of maximum sorption potential to another.

*Cation Exchange*

In spite of the fact that the base exchange properties of the crystalline zeolites have been studied since the time of H. Eichhorn (9), exact quantitative comparisons of the ease of replacement with different cations, or of the different zeolites, are very few and our total information is fragmentary. Thermochemical data are entirely lacking. Zoch (34) found that the equilibrium of the reaction between ammonium chloride and calcium stilbite (desmin) was considerably shifted by a rise in temperature from 14°C. to 50°C. More exchange took place at the higher temperature. Hence, the reaction is endothermic. He also plotted the exchange isotherm in a number of cases and found it to be a smooth curve which followed the Freundlich equation. Four calcium zeolites and one barium zeolite (harmotom) were compared as regards their ease of reaction with ammonium chloride, the order being chabazite = desmin (stilbite) > heulandite > harmotom > scolecite. The reduction in birefringence due to replacement of Ca by  $\text{NH}_4$  in desmin (stilbite) was followed optically. Subsequently, the ammonium zeolite was treated with sodium hydroxide, which restored a high birefringence. The first exchange of a single stilbite crystal against ammonium chloride solution was slow, subsequent changes were very rapid. It was observed that the first exchange produced internal cracks which facilitated subsequent penetration by solutions. Silver nitrate acted similarly.

As regards other zeolites, Gans (12) had shown earlier that natrolite and analcite were much less reactive than chabazite, heulandite and stilbite (desmin). Clarke and Steiger (8), working with fused salts at 250–300°C., showed that analcite, natrolite, scolecite, thomsonite, stilbite, heulandite, and chabazite, reacted with sodium, ammonium, barium, and strontium chlorides, and with thallium and silver nitrates, although, even at this high temperature, equilibrium was attained only slowly in certain cases. *Thomsonite* took up only 3.4 %  $\text{NH}_3$  in 24 hours.

Hey has made a detailed study of natrolite (16), mesolite (17), *scolecite* (19), *thomsonite* (15), and *edingtonite* (18). All required high temperatures, for the most part in salt fusions, for appreciable reaction. The optical properties, specific gravity, unit cell size as given by X-rays, and complete chemical analyses, are given on the products. It was shown that natrolite, mesolite, and scolecite give the same lithium derivative, indicating that they are isostructural. The X-ray data revealed that replacements often cause measurable changes in the size of the unit cell. Thallium, for instance, produced an expansion of the *edingtonite* structure.

Wiegner and Cernescu (33) carried out interesting comparisons of a kaolin clay, a permutite, and chabazite with respect to the entry of cations of different sizes. In the series Li, Na, K, Rb, Cs, they found that potassium



entered calcium chabazite relatively easily, sodium and rubidium less easily, lithium and caesium still less easily. In other words the lyotrope or hydration series shows itself from lithium to potassium, but beyond this the limited size of the channels offers a hindrance to the entry of rubidium and caesium. Using the substituted ammonias, it was found that the monomethyl ammonium ion was too large for easy entry and that the larger ions in the series were not appreciably absorbed.

These observations fall exactly as would be predicted from Hey's calculation of the radius of the pores in chabazite (1.46–1.49 Å). The rubidium ion has a radius of 1.49 Å, while caesium is 1.65 Å. Both are excluded. Ammonium ( $r = 1.43$  Å) can enter, but monomethyl ammonium ( $r = 2.59$  Å) cannot.

Complete exchange isotherms have been obtained in very few cases. Vanselow (30) studied the entry of Na and K into heulandite and analcite in relation to concentration.

It is highly significant that in the anhydrous channels of the ultramarines the small monovalent ions enter in the order  $\text{Li} > \text{Na} > \text{K}$ , whereas in the hydrated channels of chabazite we have  $\text{K} > \text{Na} > \text{Li}$ , which is the usual order also for external surfaces in aqueous colloidal systems.

#### *Action of Acids*

The zeolites are readily decomposed by strong acids, leaving a residue of silica. This action has been the subject of considerable discussion since, in certain cases, a coherent silica skeleton remains as a pseudomorph. Such structures show birefringence which may even persist after ignition. Hey (13), in a discussion of the earlier work, points out that coherent silica pseudomorphs are probably formed in all cases where the original Si/Al ratio exceeds 3, since the solution of the Al cations would still leave, on the average, a three-dimensional network. This is equivalent to the statement that the framework charge ratio should not exceed 0.250. This accords with the fact that stilbite, heulandite, and chabazite most readily form these oriented silica gels.

The action of dilute acids and of acid-reacting salts leads to loss of aluminum as well as of the exchangeable bases, and eventually silica only remains. However, Kappen (20) showed that, if the quantity of acid is insufficient to react with all the exchangeable bases, then, after washing, the products will liberate acids on treatment with neutral salts. The silica skeleton produced when excess acid is used has no such power. Table VI gives some of Kappen's results, recalculated to show the relation between the acid used and the exchangeable bases in the chabazite.

These results indicate that chabazite exerts a real or apparent acid

function after incomplete reaction with acid. The nature of this reaction, as Kappen showed in other experiments, was not purely an exchange of calcium, *etc.*, for hydrogen, but involved also losses of aluminum. Natrolite, analcite, and stilbite (desmin) showed similar properties to chabazite but gave smaller exchange acidities. It would seem, therefore, that hydrogen zeolites are completely unstable in the free state, but hydrogen or aluminum zeolites may have a limited range of existence in partial replacement. On treatment with neutral salts, the exchange acidity produced is found to be approximately equivalent to aluminum, which appears simultaneously. It is possible, therefore, that this aluminum is directly exchanged from the zeolite, and that the acid-treated chabazite is really a calcium-aluminum-hydrogen zeolite in which all three cations exchange.

TABLE VI

*Exchange Acidity of Chabazite Treated with HCl at 50°C., Washed with Water, and Shaken with 100 cc. N KCl*

(5 g. chabazite contained 15.48 m.e. Ca + K + Na originally)

HCl concentration	HCl milliequivalents	Exchange acidity milliequivalents
0.01	1.0	0.10
0.02	2.0	0.20
0.05	5.0	0.38
0.10	10.0	0.42
0.20	20.0	0.00
3.00	300.0	0.00

#### *Electrochemical Properties*

Günther-Schulze (25) and Weigel (32) made observations on the electrical conductivity of the zeolites. The former came to the conclusion that the exchangeable cations were responsible for the conductance, whereas the latter ascribed it chiefly to the water. Their experiments, however, were by no means comparable.

The fact that thin plates ground from single crystals of chabazite act as cationic sieve membranes strongly suggests that Günther-Schulze was right. This property of zeolitic crystals was investigated by Marshall (23), using chabazite and apophyllite (the latter is not a true zeolite). It was shown that, when such plates are used to separate salt solutions of different concentrations, potential differences are set up (Table VII). These approach the theoretical potentials calculated on the assumption that the cations are mobile but the anions immobile. At very low concentrations ( $N/10,000$ - $N/1000$ ), liberation of cations by hydrolysis of the zeolite upsets the results. At high concentrations ( $> N/10$ ) the potentials are lower than

the theoretical. This may be due to some anionic conductance through the membrane. It is evident that a membrane permeable to cations and to water molecules would also be permeable to OH ions, even if large anions were completely excluded by the small size of the pores. Experiments confirmed this conclusion—calcium hydroxide gave very low potentials. Since very large cations cannot pass through zeolite structures, salts of such cations might be expected also to give low potentials. This was found to be the case with benzyltrimethylammonium chloride (Triton B chloride). In such solutions some cationic conductance across the membrane still occurs—partly due to hydrogen and partly to surface reactions between the exchangeable ion of the zeolite and that of the outer solution. The chabazite and apophyllite membranes were sensitive both to monovalent and divalent ions; the latter gave the better results at very low concentrations, probably due to reduced membrane hydrolysis.

TABLE VII

*Typical Potentials Obtained Using Thin Chabazite  $[(\text{CaNa}_2)\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}]$  and Apophyllite  $[\text{KF} \cdot \text{Ca}_4\text{Si}_8\text{O}_{20} \cdot 8\text{H}_2\text{O}]$  Plates*

Mineral	Solutions	Potential observed millivolts	Potential calculated assuming immobile anion millivolts
Chabazite	N/1000-N/100 KCl	51.3	57.5
	N/1000-N/100 $\text{CaCl}_2$	21.8	27.2
	N/1000-N/100 (Triton B)Cl*	27.5	57.5
Apophyllite	N/1000-N/100 KCl	54.6	57.5
	N/1000-N/100 $\text{CaCl}_2$	24.0	27.2
	N/1000-N/100 $\text{Ca}(\text{OH})_2$	6.5	27.2

\* Triton B is benzyltrimethylammonium.

Theoretically, such membranes should provide a means of determining unknown activities in solutions containing single mono- and divalent cations. In practice, several difficulties arise; the plates must be entirely free from microscopic cracks, hence perfect crystals must first be found; cracks develop in time between the crystal plate and the cement which holds it to the glass tube; asymmetry potentials between the two faces of the plate often persist for long periods; finally, resistances upwards of 100 megohms are the rule. These difficulties have now been overcome by the use of clay membranes, whose properties are described later in Chapter 14.

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## CHAPTER 5

### THE STRUCTURES OF SILICATES WITH PLANAR FRAMEWORKS

Before taking up individual members of this group, certain general features common to all are to be considered. The first is the nature of the silica sheets. Fig. 7 shows a contact model in which all the silicon atoms lie on the same side of the hexagonal network of oxygen atoms. Only three valencies of the silicon are concerned in this sheet; the composition is therefore  $(\text{Si}_2\text{O}_3)^{++}$ . The fourth silicon valency is directed at right angles to the plane of the sheet. It also is satisfied by oxygen, which then serves to link up other sheets. If this oxygen is regarded as belonging to this same silicon we have a composition  $(\text{Si}_2\text{O}_4)^{-}$ . Since, however, oxygen atoms are so much larger than silicon, this is equivalent to a second sheet practically equal in thickness to the first. The silicon atoms fit into the tetrahedral space enclosed by four oxygens. In most cases the fourth oxygen forms part of another unit of the structure, namely, a double sheet of moderately close packed oxygens enclosing aluminum or magnesium atoms in octahedral spaces formed by six oxygens. This double layer is shown in Figs. 15 and 16.<sup>1</sup> Pauling (18) first pointed out that the close correspondence in unit cell size between the silica sheet and the double alumina or magnesia sheet is responsible for this being a favored structure among the aluminosilicates. Aluminum atoms may reside in two different environments in the same mineral: first, in tetrahedral spaces where Al substitutes for Si just as in the feldspars and zeolites; secondly, in the octahedral spaces where the situation is similar to that of the Al in gibbsite— $\text{Al}_2(\text{OH})_6$ .

Certain variants of the silica sheet are also known. The free compound  $(\text{Si}_2\text{O}_6)\text{H}_2$ , which would be a silicic acid, has at best only a transient existence. One derivative, however, is the mineral apophyllite. The  $\text{Si}_2\text{O}_3$  sheet is no longer hexagonal, but consists of alternate rings of four and eight tetrahedra (Fig. 17). Furthermore, the silicon atoms are found in alternate groups on both sides of the sheet. The charged structure  $[(\text{Si}_2\text{O}_4)^{-}]_n$  is compensated by  $\text{Ca}^{++}$ , but potassium and fluorine atoms and water molecules or  $\text{OH}-\text{H}$  groups are all incorporated between the layers, giving

<sup>1</sup> To facilitate the construction of the models, some simplifications were used. The most serious of these is found in the octahedral layers where two layers of oxygen atoms or OH groups enclose Al or Mg. Actually, the packing of the O and OH is more open than that depicted in Figs. 15, 16, 20, 21, 22, and 23. The true situation can be seen in Fig. 24, representing attapulgite, where the octahedral layers which here occur in strips are precisely to scale.

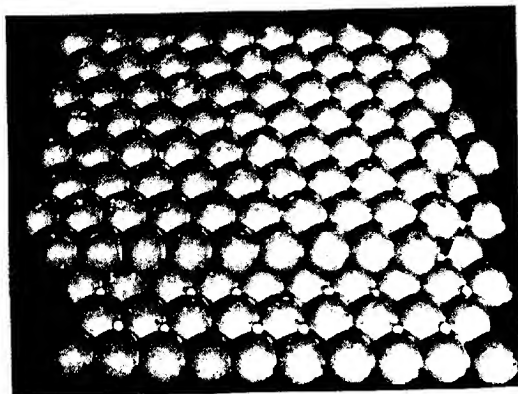


Fig. 15. Double layer of hydroxyl groups enclosing aluminum in octahedral positions, gibbsite unit  $[\text{Al}_2(\text{OH})_6]$ . The layers are staggered to show that two-thirds of the octahedral positions are filled by Al. Actually, the hydroxyl groups are not in closest packing as shown and the Al atoms shown are relatively too small.

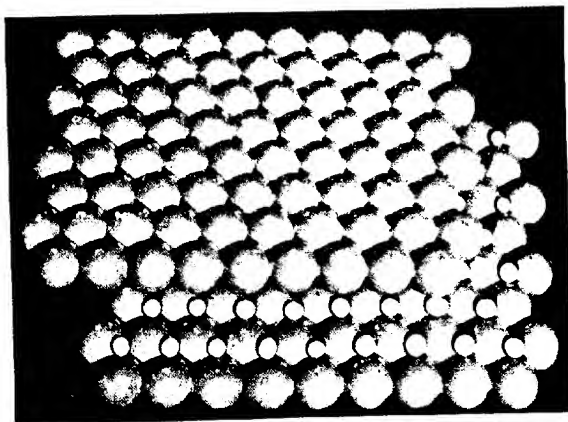


Fig. 16. Unit of brucite structure  $[\text{Mg}_2(\text{OH})_6]$ , similar to that of gibbsite, except that all octahedral positions are occupied by magnesium. The hydroxyl groups are actually in a more open packing than that shown.

$\text{Ca}_4(\text{Si}_6\text{O}_{20}) \cdot \text{KF} \cdot 8\text{H}_2\text{O}$ . The framework has thus a very high charge, but it arises quite differently from that of the zeolites. The intense polarization of

the water molecules in this structure is very striking. Nevertheless, apophyllite shows an essential similarity to the zeolites in that hydration and dehydration occur continuously and reversibly. Base exchange is exceedingly sluggish, but the use of apophyllite as a cationic membrane electrode suggests that in its exchange properties it differs in degree, but not in kind, from the zeolites.

A less drastic modification of the silica sheet is believed to form the basis of structure of certain fibrous clays—attapulgite and perhaps also sepiolite (meerschauum). The  $\text{Si}_2\text{O}_3$  layer retains its hexagonal character but the Si atoms are grouped in strips, first on one side and then on the other (Fig. 18). The alumina-magnesia layers are, therefore, also in strips to correspond. This structure is dealt with in some detail below.

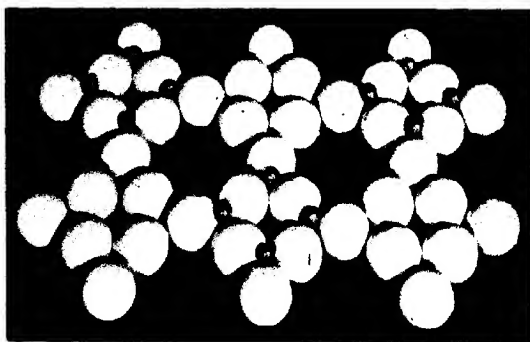


Fig. 17. Tetragonal silica sheet  $[(\text{Si}_2\text{O}_3)^{2-}]_n$ . Only the silicon atoms on the upper side of the oxygen layer can be seen. Apophyllite has a distorted form of this sheet.

In the structure originally proposed (17) for the clay mineral halloysite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ), intact hexagonal  $(\text{Si}_2\text{O}_3) (\text{OH})_2$  units were combined with  $\text{Al}_2(\text{OH})_6$ , the layers being held together only by auxiliary valency forces.

However, this particular structure is probably incorrect, as we shall see later. In discussing the structure of the mineral euclase, Bragg (4) states "It appears to be a general rule in silicates containing hydroxyl that the OH group should not be linked to silicon."

Hendricks (9) has suggested that the silica-rich kaolin mineral known as anauxite is composed alternately of kaolinite layers and double silica layers. One could imagine the latter to be derived from two  $\text{Si}_2\text{O}_3$  layers joined through oxygen, giving  $\text{Si}_2\text{O}_3 \cdot \text{O}_2 \cdot \text{Si}_2\text{O}_3$ . Such a triple layer (Fig. 19) would



have the same *C* axis spacing as kaolinite, and mixed lattices containing both constituents would appear largely as kaolinite itself, insofar as X-rays

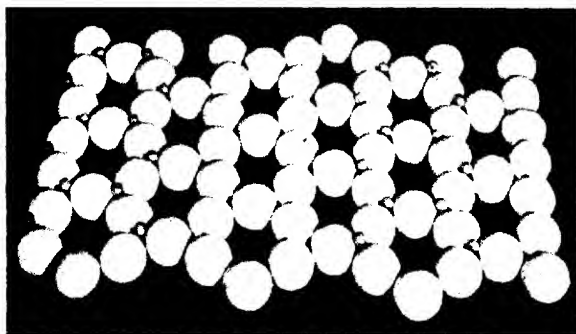


Fig. 18. Silica sheet  $[(\text{Si}_2\text{O}_5)^{2-}]_n$  as in attapulgite. The silicon atoms are in strips alternately on the two sides of the oxygen sheet.

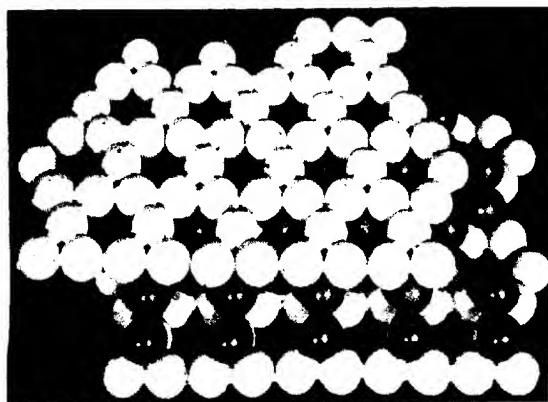


Fig. 19. Double silica layer  $[(\text{Si}_2\text{O}_5, \text{O}, \text{Si}_2\text{O}_5)]_n$  believed to occur interleaved with kaolinite layers in anauxite (Hendricks). The oxygen atoms connecting the two layers are shown dark. The silicon atoms are not shown.

are concerned. In this way the various compositions from  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  may be explained.

A somewhat expanded silica layer, in which about half of the silicon is replaced by ferric iron, forms the basis of Hendrick's structure of cronstedite (11) an iron analog of kaolinite. The rare well-crystallized mineral amesite, according to Gruner (8), also has this expanded kaolinite unit. The enlarged Si layer carries a strong negative charge due to substitution of half the Si by Al. This is balanced in the Al layer by an appropriate amount of aluminum with magnesium and ferrous iron.

For convenience in classification, the clays and related minerals are divided into four groups—the kaolin group, the hydrated mica group, the expanding lattice group, and the attapulgite or fibrous group. The colloidal

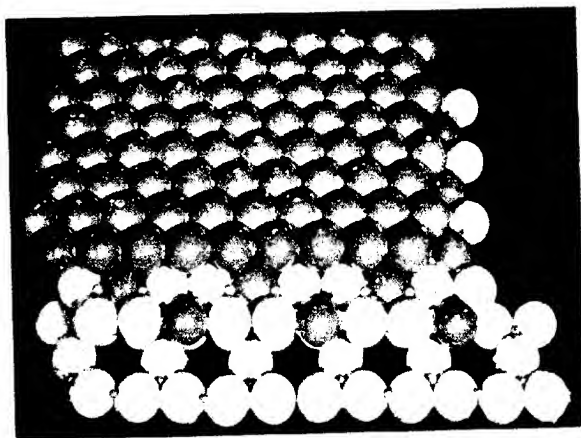


Fig. 20. Main features of the kaolinite, dickite and nacrite structures. The oxygen atoms are white, the OH groups grey. The layers are staggered to show the Si and Al atoms. The packing of the oxygen and OH in the octahedral layer is actually less close than is here depicted.

chemical properties cut across these divisions to some extent. For each mineral, therefore, the particular combination of factors leading to the colloidal character will be stressed.

#### *The Kaolin Group (1:1 Lattice Type)*

One silica and one alumina layer are present. Kaolinite, as mentioned above, varies somewhat from the ideal composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  which can be written as  $\text{O}_5\text{OH}$ . Besides the silicious anauxites, alumi-  
 $\text{Si}_2\text{O}_3$   
 $\text{Al}_2(\text{OH})_3$

nous kaolinites are also known. The latter are apparently compensated internally in some way, since no other cations than Al, Si, and H are found. Nacrite and dickite correspond very closely to the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . The three minerals differ structurally only in the manner of stacking the lattice units. Kaolinite is now believed to be triclinic (5), whereas dickite and nacrite are monoclinic. In consequence, the general properties are very similar. As far as the colloidal properties go, only kaolinite has been studied. The most important features common to all these structures are displayed in Fig. 20, in which the sheet units are easily distinguished. There appears to be no room for penetration of ions or small molecules between the sheets. Thus, the colloidal character would

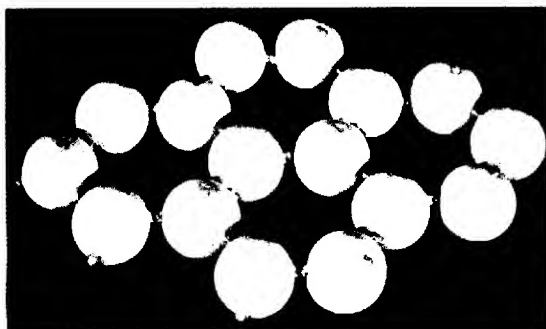


Fig. 21. Water layer of endellite (hydrated halloysite) according to Hendricks and Jefferson (10). Hydrogens are indicated by small beads. Those on the upper side of the network form hydrogen bonds with oxygen of the  $\text{Si}_2\text{O}_5$  layer of kaolinite. Kaolinite units and water layers alternate regularly.

seem to be associated rather with the external surfaces than with internal reactions. The flat external surfaces of the 001 planes would seem to be relatively inert, although, like all relatively inert surfaces, they should show adsorption properties. The edges of the particles, however, comprise unsatisfied valencies which lead to ionization and exchange reactions, both cationic and anionic.

Halloysite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ; also known as hydrated halloysite, recently (1) renamed endellite) and metahalloysite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ; also known as halloysite) are important members of the group, although little work has been done on their colloidal properties. Mehmeli (17) ascribed to halloysite a structure which is simply obtained by stacking together alternate  $\text{Si}_2\text{O}_5(\text{OH})_2$  and  $\text{Al}_2(\text{OH})_6$  units. On dehydration, water was sup-

posedly lost between the OH of the silica layer and that of the alumina layer, leaving a structure apparently similar to those of kaolinite, nacrite and dickite.

Hendricks and Jefferson (10), however, have found that the X-ray data accord better with an alternation of kaolinite-like layers with double layers of water molecules, some disorder being present in the stacking (Fig. 21). This has received strong support from MacEwan's (13) and Bradley's (3) observation that ethylene glycol will replace part of the water of endellite. One-half of the water molecules can be replaced by a single molecular layer of the glycol.

The distinction between endellite, which has lost its interlayer water to give  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and kaolinite seems to be a matter of perfection of stacking. Although endellite undoubtedly has a true layer lattice it forms long rod-shaped particles instead of plates, and on dehydration this shape is retained.

#### *The Hydrated Mica Group (2:1 lattice type)*

Two groups of minerals are included under this heading. The sericite, bravaisite or illite group (6) consists of somewhat hydrated potash micas in which increase in hydration is accompanied by decrease in potassium. The dehydrated end member is, therefore, close to muscovite. The limits of variation are by no means well established. The vermiculites (7) are characterized by a more definite stage of hydration in which layers of water molecules of definite thickness alternate with the aluminosilicate units. They are related chemically to the magnesium-iron micas, the biotites. Interstratifications of vermiculite and anhydrous mica units sometimes occur; these are grouped under the name hydrobiotite. Fig. 22 illustrates the structural scheme of muscovite. The  $\text{Si}_2\text{O}_5$  layers carry a charge due to the substitution of Al for Si. In muscovite and the illite group this is accounted for by potassium atoms which are partially embedded in the  $\text{Si}_2\text{O}_5$  layers and can be regarded as acting like a cement between adjacent aluminosilicate units. In the vermiculites a similar replacement is compensated largely internally; that is, the negative charge on the silica layers is balanced by a positive charge on the alumina sheet, which contains an excess of divalent and trivalent cations. It must be noted that in the simplest Al layer only two-thirds (4) of the octahedral positions are taken. There is room



for two more cations to bring the total to six. Pyrophyllite  $\text{Al}_2\text{O}_4(\text{OH})_2$  and



talc  $\text{Mg}_3\text{O}_4(\text{OH})_2$  may be considered as the simple unsubstituted prototypes



of the micas. The mica group is noteworthy for the wide variety of substitutions which can occur. It is unfortunate that so little is known of the colloid-chemical properties of the vermiculites, since these are found in large amounts in relatively pure condition. They show continuous dehydration curves with irreversible collapse to give talc-like material at high temperatures. No base exchange data are available. The illite group is in some respects better known in spite of the fact that only the colloidal fractions are homogeneous.

*The Montmorillonite or Expanding Lattice Group. (2:1 lattice type)*

Our knowledge of this group has increased very rapidly since 1933 when Hofmann, Endell and Wilm (12) first demonstrated the variable *C* axis

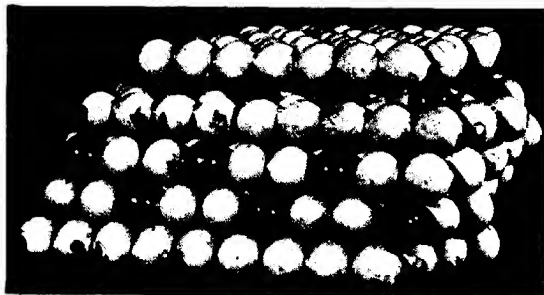


Fig. 22. Structure of muscovite mica. The upper black spheres represent potassium atoms which link one unit to the next. The topmost silica sheet belongs to the next unit layer. The oxygen and OH of the middle octahedral layer are actually in a more open packing than that depicted.

length, which changed with water content. They related the chemical composition to that of pyrophyllite. The units are essentially the same as in the micas, but, as will be shown later, the  $\text{Si}_2\text{O}_5$  layers carry smaller charges. Molecules of high dipole moment are able to penetrate between the lattice units. Fig. 23 illustrates the general structural features. Marshall first (16) reconciled the chemical compositions of different members of the group with this structure by placing the exchangeable cations along with water molecules in the variable spacings between adjacent aluminosilicate units. This deduction was shown to accord with the fact that the cation exchange capacity varies little with particle size (15, 16), and with the evidence of double refraction by electrical orientation, which showed that the exchangeable cations were anisotropically distributed within the clay particles (14, 15).

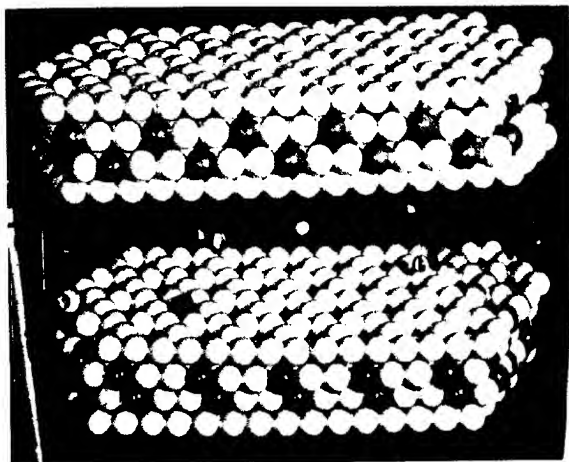


Fig. 23. Structure of the montmorillonite clays. The water molecules between the layers are omitted. The small suspended spheres between the unit layers represent exchangeable cations such as calcium or sodium. A "fixed" potassium atom can also be seen as the black sphere associated with the  $\text{Si}_2\text{O}_5$  layer. The packing of the oxygen and OH in the octahedral layer is actually less close than is here depicted.

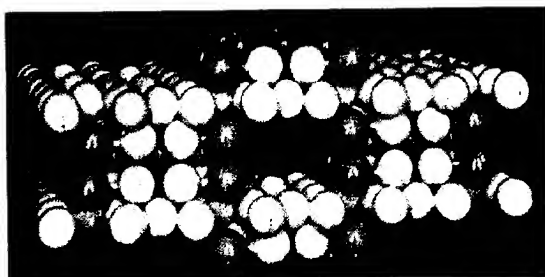


Fig. 24. Structure of attapulgite (Bradley). The model actually represents the magnesium end member, all octahedral positions being occupied by Mg atoms (beads). Associated with Mg are oxygen, hydroxyl and water.

A number of specific mineral names are now used to denote members with different chemical compositions. We shall use the general classification of Ross and Hendricks (19). The limits for each species are not yet firmly established. Montmorillonite, which gives the name to the whole group, is

used specifically for material in which some Al from the middle layer is replaced by Mg. Beidellite has a predominant replacement of Al for Si. Nontronite has a large replacement of Al by Fe. Saponite (magnesium bentonite, magnesium beidellite) has a large replacement of 3 Mg for 2 Al, but the lattice charge arises chiefly by substitution of Al for Si. Details of the variation in properties with changes in chemical composition are discussed in part under "Interpretation of Chemical Analyses" and in later sections under specific properties.

#### *The Fibrous Clay Group (Palygorskites)*

The structure of attapulgite as determined by Bradley (2) is seen in Fig. 24. The silica sheets are in a sense continuous, but the silicon atoms occur in strips arranged alternately on either side of the oxygens. The fourth valency of the silicon links the sheet with the alumina-magnesia sheets which are in strips to correspond. It will be seen that channels of fixed width, running parallel to the strips or amphibole chains, are present. The *a* axis of attapulgite corresponds to the *c* axis of the micas. In attapulgite itself the silica layer carries only a small replacement of Al for Si; the main substitution is 3Mg for 2Al in the alumina strips. The magnesium end member is given the formula  $(\text{OH})_2\text{Mg}_3\text{Si}_5\text{O}_{20} \cdot 8\text{H}_2\text{O}$  by Bradley, four of the water molecules being in the structural channels. This end member is presumably identical with sepiolite (meerschauum), although little is known of the latter from the structural standpoint. The analyses of attapulgite thus far available show about equal numbers of Al and Mg atoms in the hydrated alumina-magnesia strips.

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*Note added in proof.* The composition and exchange reactions of vermiculites have recently been studied by J. Barshad [*Am. Mineral.* **33**, 655 (1948)]. A high exchange capacity was found, the exchange cation being chiefly Mg (sometimes also Ca). These cations take the place of the K in biotite, and upon replacement by potassium the interlayer water is lost and the product is apparently identical with biotite. The reverse change was also effected.



## CHAPTER 6

### THE STRUCTURAL INTERPRETATION OF CHEMICAL ANALYSES OF THE CLAY MINERALS

Because of the wide degree of isomorphic replacement possible in the clays and the micaceous minerals generally, the structural interpretation of analytical results is especially interesting. In one respect, however, the situation is no different from that found in the chemistry of all crystallizable materials. Before confidence can be placed in any interpretation of the analysis, proof of essential purity must be forthcoming. This is not the place to discuss the relative advantages of different methods of testing the homogeneity of finely divided materials like the clays. The list includes X-ray diffraction, electron microscopy, differential thermal analyses, dehydration curves, refractive index determinations (on single particles or on aggregates), measurements of the electrical double refraction of suspensions, determinations of specific gravity, fractionation according to particle size, fractionation according to specific gravity, determination of cation exchange capacity, characteristics of titration curves. In general, several methods must be used to attain any degree of certainty as to purity. The most powerful now begin with a fractionation according to particle size. The various fractions are then examined and characterized by physical methods, and are finally analyzed chemically. If several fractions have identical physical properties and give closely similar chemical analyses, then this is strong presumptive evidence of purity. It is unlikely that a fine-grained impurity would show exactly the same particle size distribution as the main constituent. The most difficult cases are mixtures of the clay minerals amongst themselves, since impurities such as quartz and feldspar with their greater tendency to the formation of large crystals are generally found in the coarser fractions.

The occurrence of mixtures of clay minerals is exceedingly common. It accounts for the large number of proposed species names which have now passed into obsolescence. This is less surprising than the insight which some early investigators displayed, despite inadequate methods of recognition, in their emphasis upon certain characteristic types. Dufrénoy in his "*Traité de Minéralogie*" (2nd Ed., Paris, 1856), distinguishes very clearly between the kaolins, the halloysites, and the fullers earths. He also studied nontronite, which we now know as the iron-rich member of the montmorillonite group. We may conclude that the extreme degree of subdivision found amongst the clay minerals does not obliterate their distinctive macroscopic

properties. From the time of Dufrénoy to the 1920's, few mineralogists of repute concerned themselves for long with the clays. The modern outlook is based on the combined application of precise microscopic methods and complete chemical analyses, later amplified by X-ray techniques, by C. S. Ross and others in the U. S. Geological Survey, since 1924.

The interpretation of clay mineral analyses described below was devised by the author in 1935. At that time the first quantitative fractionations had been accomplished (10, 11) and, in the case of a Wyoming bentonite (montmorillonite) and Putnam clay (beidellite), several of the finer fractions appeared homogeneous. At the same time, X-ray results obtained by Hofmann, Endell and Wilm (montmorillonite), and Hofmann and Bilke (Putnam clay), showed that both belonged to the same group, characterized by the variable *c* axis spacing and a 2:1 layer lattice. The chemical compositions, however, were so different from each other, and from the idealized composition  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ , that the author felt that some plausible substitutions<sup>1</sup> had to be invoked to bring the X-ray and chemical evidence into agreement. It was found that the substitution of  $\text{Al}^{+++}$  cation for Si in the Putnam clay fractions served this purpose. The cations which balanced the negative charges on the  $\text{Si}_2\text{O}_5$  layers had then to be accommodated. It was realized that they were largely comprised of the exchangeable ions and that the layers of water molecules separating the aluminosilicate units provided a logical site, in agreement both with the optical properties and with the relative constancy of exchange capacity with diminishing particle size. The montmorillonite fractions also showed this substitution but to a much smaller extent and a second operation, substitution of  $\text{Mg}^{++}$  cation for Al in the middle layer was tested. This combination successfully explained the analytical results, the constancy of the exchange properties, and the optical properties.

The analyses quoted by Ross and Shannon (17), and others, on montmorillonites and beidellites were then examined, using the same method of calculation, but instead of assuming that the 2:1 lattice was correct, the whole range of lattice ratios which, by the operation of these replacements would fit the individual analyses, was surveyed. (Because of the dual role of Al and of other substitutions, a given analysis frequently can be fitted to a number of possible lattice types. For instance, montmorillonite analyses generally accord with lattice ratios from 2:1 to 4:1.) It was then found that the *only* lattice ratio common to the two groups was 2:1. Hence, the chemical

<sup>1</sup> The use of the words substitution and replacement should, in this chapter, be understood as referring to comparisons between the clay compositions actually found and those of the idealized pyrophyllite or talc prototypes. No process of atomic interchange subsequent to the original synthesis is implied. The verb "to proxy" is sometimes used in this sense.

evidence could, by the use of these replacements, be brought into complete accord with the X-ray interpretations. In the Ross and Shannon analyses no base exchange capacities were given, so that it was not possible to trace the relationship between exchange capacity and lattice substitutions. However, the substitutions needed for accord with the 2:1 type were calculated, and were found to be predominantly Al for Si in the beidellites and somewhat less predominantly Mg for Al in the montmorillonites, in agreement with the author's own analyses of bentonite and Putnam clay fractions.

Since this time, many other analyses of well-defined materials have become available and in many cases data on the exchange capacity have been included. After discussing the operation of the method, we shall take up the evidence now available on predominant replacements, and on exchange capacity in relation to these replacements.

#### *Method of Calculation*

The percentage composition is first recalculated to gram-atoms of the individual elements. In the 2:1 lattice type the unit cell contains 24 oxygen atoms, four of which are present as OH groups. (In certain cases part of the OH is substituted by fluorine.) Because of the importance of oxygen as a framework atom, and since there is often no sharp distinction possible between OH groups and adsorbed water, the method originally used was to take an imaginary dehydrated unit cell with 22 oxygen atoms as the basis. The gram-atoms of oxygen were calculated from the analyses and the figures were then adjusted to correspond to the dehydrated unit cell with 22 oxygens. A simpler method (8) is to take advantage of the fact that in the idealized unit cell 24 oxygen atoms correspond to 48 cationic valencies. Of these, four belong to hydrogen, leaving 44 for silicon, aluminum and all other constituents (except fluorine which simply replaces OH and therefore does not affect the valency situation as regards the cations.) The analysis can therefore be recalculated on the basis of a total of 44 gram-equivalents of cationic constituents. A typical example is given below.

#### *Recalculation of an Analysis of Montmorillonite* Hydrogen clay, fraction 50-100 $\mu$ from Wyoming bentonite

Percentage Composition	G.-eq. of cationic constituents	G.-eq. per total of 44	Atoms per unit cell
SiO <sub>2</sub> = 54.93 + 60.06 $\times$ 4 = 3.6584		30.355	7.589
Al <sub>2</sub> O <sub>3</sub> = 21.71 + 101.94 $\times$ 6 = 1.2778		10.602	3.534
Fe <sub>2</sub> O <sub>3</sub> = 4.05 + 159.68 $\times$ 6 = 0.1522		1.262	0.421
MgO = 2.40 + 40.32 $\times$ 2 = 0.1190		0.988	0.494
K <sub>2</sub> O = 0.19 + 93.19 $\times$ 2 = 0.0040		0.033	0.033
Na <sub>2</sub> O = 0.05 + 62.00 $\times$ 2 = 0.0016		0.013	0.013
Exch. hydrogen 90 m.e. = 0.0900		0.747	0.747
		5.3030	

The next step is to compare the recalculated analysis with simplified unit cells of the 2:1 type. Two of these are  $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$  (pyrophyllite) and  $\text{Si}_4\text{Mg}_2\text{O}_{10}(\text{OH})_2$  talc. The Si layers are first completed by adding sufficient Al to bring the total number of atoms to 8. A charge is thus imparted to the Si layers; in the example given above it is 0.411 equivalents. Next the inner alumina-magnesia layer is examined. The aluminum still unassigned is added to the iron and the magnesium giving a total of 4.038 atoms which lies between 4 and 6, and is thus in agreement with the conditions laid down. In equivalents, however, there is a deficit below the theoretical value of 12 amounting to 0.381 which can therefore be regarded as the—charge on this layer. Thus we have 0.411 on the Si layers and 0.381 on the Al layer

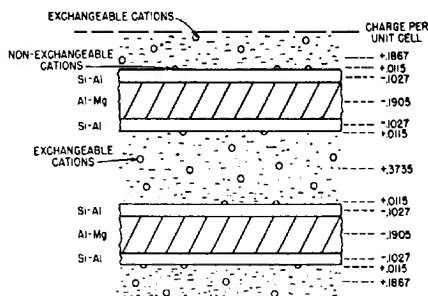


Fig. 25. Distribution of charges in a montmorillonite (Wyoming bentonite fraction 50-100 m $\mu$ ) as calculated from the chemical analysis and the cation exchange capacity.

giving a total—charge of 0.792. This charge must be neutralized by the potassium, sodium and exchangeable hydrogen, and the agreement in the two values serves merely as a check upon the arithmetic. (In the method as originally published the number of atoms in the Al layer was held at 4 and the charges were then calculated and expressed as "cations per unit cell". Part of these in the above example would be Mg, which then would be assigned to its most probable position in the inner layer.)

The next question concerns the site of the K, Na, and H which balance the negative charge on the lattice. Since the H is exchangeable, it is assigned to the interlayer water, external to the aluminosilicate framework. The nonexchangeable K and Na can be regarded as closely associated with the Si layers, since K is much too large for the octahedral positions in the Al layer. The distribution of charge is thus very completely determined, granted the assumptions. Diagrammatically it is shown in Fig. 25.

More difficult and complex cases sometimes arise. If no determinations of exchangeable cations accompany the analysis it is obviously impossible to go beyond the point of assigning apparent charges to the Si and Al layers. The way in which these are neutralized by exchangeable or nonexchangeable cations then remains undetermined. Furthermore, even though the number of atoms in the Al layer varies only between 4 and 6, the number of equivalents might lie between 8 and 18, since it is conceivable that a + charge could be acquired by the presence of more than 4 trivalent cations. Considerable guidance is afforded by the macrocrystalline micas which show a very broad range of substitutions. The work of Ross and Hendricks, discussed later, sets approximate limits to those found in the expanding lattice clays.

#### *Consideration of Results*

In Table VIII are assembled representative data on various members of the 2:1 type. In each case the original analysis was accompanied by evidence of homogeneity and base exchange data are included whenever possible. Magnesium has been assigned to the Al layer but nonexchangeable K, Ca, and Na have been listed under the heading nonexchangeable cations. It is not known whether small amounts of Ca and Na can replace part of the Mg in the Al layer, or whether they only occupy the same sites as does potassium in the potash micas. The amounts found in electrolyzed clays are not large, generally less than 0.5%, but there is no evidence that they belong to impurities. There is good evidence that lithium is present in the Al layer in certain magnesium bentonites. Nagelschmidt (14) has put forward the view that, in the montmorillonite group, Ca, Na and K do not occur as nonexchangeable ions; thus, the total lattice charge should give an exact measure of the exchangeable ions. In many cases this is true. The chief exceptions are found in the beidellites and nontronites where appreciable amounts of potassium are present, together with smaller quantities of sodium and calcium.

In comparing Table VIII with the data originally given by the author (11) for members of the 2:1 type, it must be remembered that the earlier data were calculated on the assumption that the number of atoms in the Al layer was exactly 4 per unit cell. Magnesium, ferrous iron, and manganese were placed initially in this layer to make the total up to exactly 4. In Table VIII the whole quantity of these elements present, has been placed in the Al layer. The total number of atoms thus lies between 4 and 6, and the net charges are, therefore, correspondingly less than those previously given. This can now be done because we have more data on the exchangeable ions as well as considerable information on the distribution of lattice charges in the micas. It appears that magnesium, in the micas, always occurs in the Al layers and does not function as a "cementing" ion

TABLE VIII  
Composition Data on Various Minerals

Reference and analysis number	Name	Si layers	Elements present in Al layers	Charge per unit cell in Si layers <sup>a</sup>	Non-exchangeable cations	Exchange capacity
14 [2]	Beidellite	Si, Al	Al, Fe <sup>+++</sup>	-1.08	0.00	1.08
11	Beidellite (Putnam <100 mμ)	Si, Al	Al, Fe <sup>+++</sup> , Mg, Ti	-	+0.00	.53
4 [9]	Beidellite <60 mμ	Si, Al	Al, Fe <sup>+++</sup> , Mg, Ti, Fe <sup>++</sup>	-.64	0.34	.38
14 [1]	Montmorillonite	Si, Al	Al, Fe <sup>+++</sup> , Mg	-1.49	+0.92	0.19
11	Montmorillonite	Si, Al	Al, Fe, Mg, Ti	-0.52	0.00	.94
2	Montmorillonite <200 mμ	Si, Al	Al, Fe, Mg, Ti	-0.02	0.02	.64
7 [11]	Montmorillonite 100-50 mμ	Si, Al	Al, Fe, Mg	-0.41	0.36	.75
3	Magnesium bentonite	Si, Al	Al, Fe, Mg, Ti	-0.17	0.00	.68
16 [81]	(Hectorite) <50 mμ	Si, Al	Mg, Al, Fe, Li	-0.19	0.43	.62
16 [77]	Saponite	Si, Al	Mg, Al	-1.34	+0.54	.80
3	Nontronite <50 mμ	Si, Al	Mg, Fe <sup>+++</sup> , Fe <sup>++</sup>	-0.64	+0.04	.60
16 [57]	Nontronite	Si, Al	Al, Fe <sup>+++</sup> , Fe <sup>++</sup>	-1.60	+0.96	.54
5 [1]	Illite (fine colloid)	Si, Al	Fe <sup>+++</sup> , Fe <sup>++</sup> , Al, Mg	-0.48	0.16	.64
6	Vermiculite	Si, Al	Al, Fe <sup>+++</sup> , Fe <sup>++</sup> , Mg	-1.27	-0.19	1.30
	Glauconite	Si, Al	Mg, Fe <sup>+++</sup> , Al, Fe <sup>++</sup> , Mn	-2.47	+1.24	1.23
	Glauconite	Si, Al	Fe <sup>+++</sup> , Fe <sup>++</sup> , Al, Mg	-1.83	-1.05	2.88
3	Attapulgite (0.2-0.05 μ)	Si, Al	Fe <sup>+++</sup> , Mg, Fe <sup>++</sup> , Al	-0.77	-0.39	1.76
1	Attapulgite (0.1-0.05 μ)	Si, Al	Al, Mg, Fe <sup>+++</sup> , Fe <sup>++</sup>	-0.55	+0.19	.20
			Al, Mg, Fe <sup>++</sup>	-0.23	-0.02	.07

<sup>a</sup> These figures divided by 8 give the framework charge ratios of the silica layers, comparable with those of Tables I, II and III.

between adjacent aluminosilicate units as do potassium (muscovite and biotite), calcium (margarite), and sodium. Lithium also is assigned to the octahedral layer, partly by analogy with the lepidolite micas, but mainly because there is no other way of accounting for the 2:1 structure of a lithium-containing clay now known as hectorite.

Among both the 2:1 clays and the related minerals, cases arise in which the Al layer carries a + charge which is overbalanced by a considerable negative charge on the Si layers. No examples of the converse situation have appeared. This is not surprising, since the Si layer could only acquire a large + charge by substitution of P for Si, and phosphorus is usually a very minor constituent.

The nomenclature of the clay minerals within the 2:1 lattice type is still confused, especially as regards the expanding clays. The species montmorillonite is generally restricted to members having a moderate amount, but not a preponderance, of Mg in the Al layer. Beidellite is characterized by little Mg and a considerable substitution of Al for Si, thus leading to an  $\text{SiO}_2/\text{R}_2\text{O}$  ratio of about 3. Nontronite contains a preponderance of  $\text{Fe}^{+++}$  in the Al layer. Saponite has a preponderance of Mg in the Al layer. This broad classification corresponds to the original uses of these names. Ross and Hendricks (16) subdivide the two categories, nontronite and saponite, as follows. The species name nontronite would apply to clays in which there is practically complete proxying of Al by Fe. The more aluminous members with considerable substitution of Al for Si alongside Fe for Al would be called (aluminian) nontronite. The species name saponite would be restricted to clays having Al for Si substitutions as well as a predominant replacement of 3Mg for 2Al. Another name, hectorite, would refer to a magnesium bentonite having a predominant substitution of 3Mg for 2Al, but little Al for Si, and owing its lattice charge to lithium in the Al layer.

Although there is considerable variation in composition in the expanding clay group, not all possible cases are known. Ferrous iron is usually a somewhat minor constituent, whereas in the Al layer of the glauconites it sometimes predominates. Ross and Hendricks point out that Mg and ferric iron do not occur simultaneously in quantity in the nontronites.

A very interesting zinc saponite has recently been described by Ross (15), who has revived an old name sauconite for this mineral. The new finds agree well with a zinc clay to which this name was originally given. In these clays the magnesium of saponite is almost completely replaced by zinc. Certain chromium clays, known as volchonskosites have also been described. They are apparently chromium nontronites with incomplete replacement of iron by chromium.

Thus the octahedral layer of the montmorillonite group is known to be capable of accommodating in significant amount the following ions:  $\text{Li}^+$ ,

Mg<sup>++</sup>, Zn<sup>++</sup>, Fe<sup>++</sup>, Al<sup>+++</sup>, Cr<sup>+++</sup>, and Fe<sup>+++</sup>. Chemically they have little in common, but geometrically they are all well adapted to fit the octahedral positions between two moderately close-packed layers of oxygen atoms, allowing for some mutual adjustment. Their radii vary only from 0.57 Å to 0.83 Å, while the radius of the octahedral cavity enclosed by six close-packed oxygen atoms is 0.55 Å.

The hydrous mica group is characterized by a higher negative charge per lattice unit than the expanding clay group. In Table VIII the charges range from 0.57 to 1.08 for the expanding clays, followed by 1.23 for vermiculite, 1.30 for illite, and 1.78 for a glauconite. It is unfortunate that no base exchange data are available for the vermiculites, which, standing as they do between the expanding clays and the micas, might reveal very interesting properties. As further analyses become available the exact relationship between net charge, predominant site of charge, exchange capacity and interlayer water molecules will eventually emerge.

Attapulgite, having a fibrous structure, is compared with a dehydrated unit cell of composition  $Mg_6Si_6O_{21}$ , or  $Mg_6O_6 \cdot 4Si_2O_4$ . The substitutions are relatively small. Appreciable amounts of nonexchangeable cations are present and the exchange capacity is low (13). Sepiolite (meerschaum), like attapulgite, is fibrous and has been assumed to belong to the same structural type. However, the analyses quoted by Longchambon and Migeon (9) agree better with the simple 2:1 structure than with the amphibole-like modification whose dehydrated formula is  $Mg_6Si_6O_{11}$ ; for this the silicon + aluminum is too low and the magnesium, in some cases, too high.

The calculation of lattice replacements has been almost entirely confined to the 2:1 type. The 1:1 clays deviate at times from the ideal formulae, but they contain practically no magnesium, calcium, or alkali metals, and very little iron. Their cationic and anionic exchange properties are believed to arise mainly from unsatisfied valencies at the edges of the particles.

The relationship between the site of the lattice charge, its magnitude, and the assemblage of colloid-chemical properties is at present insufficiently known. Few pure clay minerals of the montmorillonite group have been fully investigated. As will be pointed out later in dealing with the electrochemical properties, a negative charge in the Al layer causes a greater dissociation of exchange cations than does a similar charge on the Si layer. This is readily understood on spatial grounds, as was pointed out by Marshall in 1937 (12). The exchange cations associated with a charged Al layer cannot come into contact with this layer unless they are small enough to enter the "holes" in the Si layers. Thus, on the average, a physical barrier exists separating the two sets of charges in typical montmorillonites, but



not in typical beidellites. Hence, less work will be required to move the exchange cations away from the montmorillonite surface than from the beidellite or mica surface. Another way of expressing the same idea is to say that a slight departure from Pauling's rule in the case of montmorillonite is responsible for a greatly increased surface ionization.

*Detailed Composition of the Expanding Lattice Clays*

From the work of Ross and Hendricks one may now set approximate limits to the replacements found in the whole montmorillonite group. The substitution of Al for Si varies from zero up to 1.64 atoms per unit cell of 24 oxygens. The framework charge ratio of the silica layers alone thus does not exceed 1.64/8 or 0.205, which may be compared with the values given in Tables I, II and III, and with 0.25 for the muscovite and phlogopite micas. Turning to the Al layer, we find a very broad range of substitutions and of charges. Two distinct series now become apparent, differing in the total number of octahedral positions occupied, and separated by a considerable gap. In the montmorillonite-beidellite-nontronite series the number of octahedral cations varies from 4.0 to 4.5. In the saponite-hectorite and saunonite series it is almost constant at 6.0.

*Montmorillonite-Beidellite-Nontronite Series.* Starting from montmorillonites with zero charge on the Si layer and about 0.66 equivalents negative charge on the Al layer, a continuous range of replacements is found extending through clays with about 0.66 equivalents negative charge on the Si layer and zero charge on the Al layer to those beidellites having a much larger negative charge up to 1.64 equivalents, partially balanced by a strong positive charge in the Al layer. The latter arises by the presence of more than 4 trivalent cations, and may amount to as much as 1.0 equivalent. However, the total number of octahedral positions filled remains, as stated above, between the limits 4.0 and 4.5. The result is that the cations unassigned to the framework are surprisingly constant in amount. In the cases studied by Ross and Hendricks, the exchange cations, which comprise the major part of those unassigned, vary in amount only from 0.5 to 0.8 equivalents per lattice unit of 24 oxygen atoms. In most of the montmorillonites all the unassigned cations are exchangeable. As Table VIII indicates, in the beidellites and nontronites, cases arise in which cations (K, Ca and Na) are nonexchangeable. It is sometimes assumed that nonexchangeable potassium is indicative of the presence of actual mica units interleaved in a mixed lattice with the montmorillonite. However, there is no direct proof of this, and the occurrence of small amounts of non-exchangeable calcium and sodium is too well authenticated to be disregarded. As regards the nontronites, there seems to be no limitation to the proportions of iron and aluminum in the octahedral positions. The charge

on the lattice may arise either on the Si or Al layers. It appears, however, that where the iron is large in amount, magnesium is low. The exchange capacity is about the same as for other members of the series.

*Saponite-Hectorite Series.* In the saponites studied by Ross and Hendricks the charge was chiefly due to Al for Si, the replacement varying from 0.64 to 1.52 atoms per unit cell. This was partially counterbalanced by a positive charge on the Mg layer, arising from the presence of aluminum or ferric iron. The total number of atoms in octahedral positions was practically constant at 6.00. Hectorite stands apart from the other members. Its charge arises solely from the presence of lithium in place of magnesium in the octahedral positions. This lithium is, of course, nonexchangeable. The clay also contains fluorine which proxies for hydroxyl in the framework. The exchange capacities of hectorite and of the saponites are about the same as those of most montmorillonites.

In spite of the wide variation in the replacements which are needed for the interpretation of the analyses, there is only a restricted variation in total exchange capacity. In Table VIII the extremes for the expanding lattice clays are 0.38 and 1.08 equivalents per unit of 24 oxygen atoms. From Ross and Hendricks' data the figures are 0.52 and 0.79, corresponding, respectively, to 67 and 100 milliequivalents /100 g. Thus, it seems that in the original crystallization of the expanding lattice clays the three factors, lattice charge, exchange ions, and water molecules, achieve a balanced relationship. If the charge is too high or too low, fixed lattices are probably produced. These may, however, be interleaved with the expanding lattice layers giving rise to mixed lattice materials. Thus, more than one *c* axis spacing would be present. Hendricks has emphasized the likelihood of such occurrences. To learn more of these cases it is evident that what is needed is a general method for determining the quantitative distribution of lattice spacings.

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## CHAPTER 7

### THE SIZES AND SHAPES OF CLAY PARTICLES

#### *Fractionation and Particle Size Distribution*

Although certain clay deposits contain well-defined microcrystalline particles (crystals of dickite from Anglesey were measured by Miers on a goniometer), most clay minerals occur as particles too small to resolve with the ordinary microscope. Furthermore, a considerable distribution of particle sizes is frequently present. These facts hindered the quantitative development of their colloid chemistry for many years. By the use of the centrifuge and the electron microscope the experimental limitations have now largely been removed.

The qualitative fractionation of Putnam clay (now known to be essentially beidellite) by Bradfield in 1923 (2), and his study of the properties of the fractions, showed something of the enormous range of particle sizes present, and stimulated research into more precise methods. The first accurately quantitative procedure was based on a two layer principle using the tube centrifuge (11, 12). This method, devised by the author, has the advantage that, in addition to giving the distribution of particle sizes, it actually isolates fractions within predetermined size limits. It is thus merely a matter of repetition to accumulate well-defined fractions for study. The range of the method has since been extended downwards by the use of the two layer principle in the Sharples supercentrifuge (14). The range  $2\mu$ – $10\text{ m}\mu$  can thus be covered in any number of steps.

Bradfield's original procedure was amplified to give roughly quantitative fractionations by Bray (3). A mathematical examination of the sedimentation conditions in the Sharples machine has led Hauser and associates (8) to develop a procedure for quantitative fractionation which involves fewer repetitions than that of Bray.

In cases where interest is centered solely upon the distribution of particle sizes, the pipette method is frequently used. Under gravity alone it is not well suited to determinations below  $0.5\mu$ , but it can be combined with a tube centrifuge sedimentation as shown by Steele and Bradfield (21). In this way determinations down to  $50\text{ m}\mu$  have been made.

Although a considerable volume of sedimentation data on soils and ceramic materials has now accumulated, comparatively little has been done on well-defined clay minerals. It is summarized in Table IX. More information is needed on the variability of particle size distribution in pure clay minerals from different sources.

The author's detailed study (12) of particle size distribution in relation to the exchange cation showed that different members of the montmorillonite group have very different properties. In the case of Wyoming bentonite, a typical montmorillonite, dilute suspensions gave similar results, irrespective of the cation, provided the system did not undergo random coagulation. With Putnam clay, a beidellite, the quantity of the finest fraction  $<50 \text{ m}\mu$  was very much greater when the clay was saturated with Li, Na or K than with Mg, Ca, Ba or H. Distinct differences were apparent even among the Li, Na, and K clays, the order of dispersion being  $\text{Li} > \text{Na} > \text{K}$ . The H, Mg, Ca and Ba clays were not flocculated, yet they con-

TABLE IX  
*Particle Size Distribution Data on Some Well-Defined Clay Minerals*  
(Total material  $<2\mu = 100\%$ )

Reference	Clay mineral	Exchange cation	2-0.5 $\mu$	0.5-0.2 $\mu$	0.2-0.1 $\mu$	0.1-0.05 $\mu$	<0.05 $\mu$
12	Wyoming bentonite (Montmorillonite)	H	38	22	6	11	24
		Li	35	21	7	13	25
		K	33	21	11	10	26
		Ba	37	18	9	13	22
12	Putnam clay (Beidellite)	H	23	19	21	24	14
		Li	15	11	14	14	46
		K	16	13	15	23	33
		Ba	22	24	30	24	
5	{ Hectorite Nontronite Attapulgit	Na	30	16	46		8
		Na	75	12	12		1
		Na	19	51	26		3
4	{ Illite Halloysite Kaolinite		2-0.5 $\mu$	0.5-0.25 $\mu$	0.25-0.125 $\mu$	0.125-0.062 $\mu$	<.062 $\mu$
			41	21	15	10	13
			25	24	32	16	4
			46	42	5	3	3

tained, on the average, much larger particles. These suspensions showed a higher birefringence by electrical orientation than those of the Li, Na or K clays. Hence, the individual particles of the H, Mg, Ca and Ba clays must consist of oriented groups or aggregates. The process of oriented coagulation is a property chiefly of the very finest material present. In the case of the sodium Putnam clay, the lower limit of particle size is not known, but centrifuge experiments have shown that it contains about 10% of material with a settling velocity less than that of spheres  $10 \text{ m}\mu$  in diameter. Thus far, these finest particles have not been properly resolved with the electron microscope. Thus, the exact way in which they arrange themselves to form larger units in the H, Mg, Ca and Ba clays remains unknown.

A relationship between the site of predominant negative charge and the property of oriented coagulation suggests itself (13). The major factor concerned will be the possibility of two planar surfaces approaching so closely that the attractive forces between + and - layers are able to overcome the primary repulsion between the layers of cations. In the typical beidellite this will be much more easily attained than in the typical montmorillonite, where the charges are behind the silica surfaces. Hence, one would expect beidellites to show oriented coagulation more extensively than montmorillonites.

The whole concept of the characterization of a given clay by its particle size distribution needs detailed study. In the kaolinite and hydrous mica groups there is little doubt that the figures have meaning; the individually dispersed particles are relatively compact and are not broken down by weak mechanical forces in the suspension. Among the expanding clays the situation varies. The Putnam clay (beidellite) has been more extensively studied than any other, and the evidence, both from sedimentation studies and from electron micrographs of isolated fractions, shows that with a given cation the distribution curve is well defined. This was largely true of the montmorillonite from Wyoming bentonite in the author's centrifuge experiments, but Shaw (20), from electron microscope studies, concludes that breakdown to units only one lattice layer thick readily occurs. The fibrous magnesium bentonite known as hectorite is aggregated in the coarser fractions, as the electron micrographs show. Hence, its distribution curve is somewhat indefinite. The fibrous clay attapulgite shows this behavior to an extreme degree.

The electron microscope has now provided a direct method for the observation of the sizes and shapes of clay particles. A preliminary fractionation by the centrifuge is highly advantageous in interpreting the results where mixtures may occur. In general, the earlier conclusions of a predominantly platy structure based on indirect methods (dityndallism and birefringence effects during flow) are confirmed. The electron microscope, however, has revealed a lath-like, or even a rod-like character in two cases where it was unsuspected, halloysite and hectorite. Nontronite was previously known to be lath-like from ordinary microscopic observations. Thus, we now have a number of cases in which an elongated crystal habit arises in minerals with a planar lattice structure. Apropos of nontronite and hectorite, Ross and Hendricks (18) point out that the undisturbed material, examined optically, shows perfect micaceous cleavage. "Thorough dispersion, however, does produce ribbons, which appear to have been absent in undisturbed material. This difference in habit between nontronite and hectorite, as compared with montmorillonite, seems to be analogous to that between chrysotile asbestos and kaolinite, which has

been investigated by Warren and Hering (1941) and discussed by Hendricks (1942). These studies indicate that the greater size of the Mg ion results in a strain within the crystal lattice, which restricts the width of the layer to a few units of structure. Growth along the length of the plate, however, is still permitted; in other words, the strain is taken up in one direction. In the same way the ribbon-like habit of nontronite and hectorite seem to be due to the greater ionic radii and the strain produced by ferric iron and magnesium, resulting in a structure giving potential cleavability perpendicular to the micaceous plates."

Since the clays all have the crystal habits of plates, laths, or rods, the usual Stokes' Law formula for spherical particles provides only a very crude approximation to their settling behavior. In fractionations, it is customary to arrange the limits according to equivalent spherical diameters. Nonspherical particles, however, have more than one equivalent spherical diameter, depending upon the orientation of the particle with respect to the force acting upon it. The question as to whether or not fractionation procedures cause orientation of the particles is thus important. Marshall (12), by applying considerations of kinetic energy, concluded that, in the tube centrifuge, orientation would only be appreciable for the fraction  $2\text{ }\mu\text{-}1\text{ }\mu$ , and even in the more intense field of force of the Sharples supercentrifuge particles with equivalent spherical diameters smaller than  $0.5\text{ }\mu$  would hardly be affected. This follows also from the very rapid increase in rotational Brownian movement with diminishing particle size. Kelly and Shaw (10), in discussing electron micrographs of the lath-like particles of halloysite, concluded that an overlapping of fractions was probably caused by orientation during fractionation.

Before the advent of the electron microscope the only methods for the determination of particle shape were indirect. The author (15) employed four steps as follows:

- (1) A careful fractionation was carried out using the two layer method.
- (2) Stable suspensions of the various fractions were made to flow and, from the dityndallism, the general shape character was deduced.
- (3) By making ultramicroscopic counts on suspensions of known concentration the mean particle volumes were determined.

- (4) Platy particles were approximated to oblate ellipsoids of rotation of axial lengths  $a$  and  $b$  ( $a < b$ ). The volume  $V = 4/3ab^2$  and the sedimentation velocity under gravity  $v = 2/9 \frac{ab(D-d)g}{F\eta}$ , where  $\eta$  is the viscosity of the liquid,  $D$  and  $d$  are the densities of solid and liquid respectively,  $g$  is the gravitational constant and  $F$  is a shape factor. The values of  $F$  were tabulated by Marshall (12) for particles of various shapes, based on formulae given by Müller (17). It appeared that

$F$  was practically constant for oblate ellipsoids. Kelly and Shaw (10) have since shown that Müller's formula was in error and that the  $F$  values converge less rapidly to a constant value with increasing eccentricity, than the author found. However, a good approximation for very thin plates can still be had by putting  $F = 0.66$ . On applying this method to the fraction 100-50 m $\mu$  of the Putnam clay (beidellite) we find  $2a = 7.3$  m $\mu$ ,  $2b = 670$  m $\mu$ ,  $b/a = 92$ . In the case of rod-shaped particles,  $F$  does not converge and the method breaks down.

The use of the electron microscope has greatly simplified determinations of shape and size. Two dimensions can be determined directly and the third remains to be found. Since clay particles generally lie flat upon the collodion support, this undetermined third dimension represents the thickness of the plate or lath. It may be deduced by combining sedimentation or ultramicroscopic data with the visible dimensions and some guidance as to its order of magnitude can also be obtained by considerations of electron penetration (16). For the Putnam clay fraction 100-50 m $\mu$ , previously referred to, the mean plate diameter determined directly was 373 m $\mu$ . By combination with the mean sedimentation velocity, the thickness was found to be 11.2 m $\mu$ . Thus, the agreement between the indirect and the direct methods is only approximate; for exact agreement a much narrower fractionation would be needed.

#### *Kinetics of Coagulation*

The experimental verification of Smoluchowski's theory of coagulation for spherical particles has had an interesting consequence. We can now say with certainty that, in the region of quick coagulation, where all collisions lead to union, particles must come into contact or practically so, before they adhere. Action at a distance is excluded by the results (21). If this is true for spheres, irrespective of their chemical nature; it should also be true for particles having other shapes. The mathematical problem, for the case of nonspherical particles, thus reduces itself to the determination of the probability of collision. Müller (17) has examined the situation for plate- and rod-shaped particles, taking into account the translational, but not the rotational, Brownian movement. For thin plates, treated as oblate spheroids, he found that the rate of coagulation should be about 50% greater than for an equal number of spheres. This agrees well with Tuorila's observations on kaolin clays, since values of  $A/r$  between 2.5 and 3.0 were commonly found, as compared with 2.0 for spheres (22). ( $A/r$  is the ratio of the hypothetical attraction radius  $A$  to the true radius  $r$  for a spherical particle.) For long rods of  $V_2O_5$  and benzopurpurin 4B Wiegner and Marshall (23) found much higher values of  $A/r$  than Müller's



theory predicts, due probably to his neglect of rotational Brownian movement. Now that shapes may be determined with the electron microscope it would be interesting to carry out further experiments on both platy and rod-like clay particles.

#### *Electron Micrographs of the Clay Minerals*

A considerable volume of work has now been published on the appearance of individual clay particles in the electron microscope. The prepara-



Fig. 26. A dickite crystal (Humbert and Shaw, 9).

tions are made by allowing a dilute clay suspension in water to evaporate on a thin collodion film. After being placed in the instrument under a high vacuum the particles probably become dehydrated. This reduces the thickness of particles of the swelling clays and, in the case of endellite (hydrated halloysite), it is probable that the irreversible change to halloysite occurs.

*Dickite* (Figs. 26 and 27). The beautifully crystalline character is well shown in two aspects of the same crystal obtained when the collodion support split and curled (Humbert and Shaw, 9).

*Kaolinite* (Figs. 28 and 29). Electron micrographs of this mineral were first obtained by Eitel and others (6). Fig. 28, by Shaw and Humbert (19), shows a typical sample from a relatively pure deposit, whereas Fig. 29 illustrates the smaller particle size and the less perfect outlines found in a kaolinitic soil (Cecil clay).



Fig. 27. The same dickite crystal as Fig. 26, now seen on edge. (Humbert and Shaw, 9.)



Fig. 28. Kaolinite from Jerome, Arizona. (Shaw and Humbert, 19.)



Fig. 29. Kaolinite as found in the Cecil clay. (Shaw and Humbert, 19.)

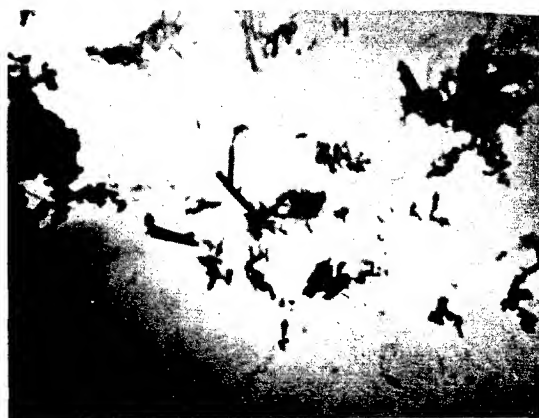


Fig. 30. Halloysite and endellite. (Lawrence County, Missouri.) (Marshall and Dufford — unpublished.)

*Halloysite and Endellite* (Fig. 30). The rod-like character of halloysite particles was unsuspected until Shaw and Humbert (19) examined a sample from Maiden, N. C. They drew attention also to the split character of many of the rods, evidenced by notches at the ends and occasionally



Fig. 31. Illite. (From Illinois Graptolite.) (Marshall and Dufford—unpublished.)

by a light streak down the middle. There appears to be some tendency toward a lath-like shape, but the two smallest dimensions do not differ very markedly. Axial ratios appear to be predominantly in the range 5:1 to 20:1.

*Illite (Bravaisite, Hydrous Mica)* (Fig. 31). Shaw and Humbert's (19) original electron micrograph showed aggregated material made up of small plates. In Fig. 31 (Marshall and Dufford) better dispersion was secured

and the sample is seen to be made up of very thin plates together with thicker units of about the same area.

*Beidellite* (Figs. 32-34). The type mineral from Beidell, Colorado, gave rather poorly defined particle shape or size (Shaw and Humbert, 19). Fig. 32, by Marshall and Dufford, illustrates this also. However, Putnam



Fig. 32. Beidellite, (Beidell, Colorado.) (Marshall and Dufford (unpublished).)

clay on fractionation showed a well marked gradation in particle size, the units being fairly thin plates with indented or irregular outlines. The fraction 100-50  $m\mu$ , Fig. 33, shows this character (Marshall *et al.*, 16). The finest material, < 20  $m\mu$ , shows a mixture of thick and thin units in aggregation, the smallest particles being inadequately resolved. The largest particles present, corresponding to 20  $m\mu$  equivalent diameter, are around 75  $m\mu$  in diameter, the calculated thickness being about 5  $m\mu$ .

*Nonttronite* (Fig. 35). Shaw and Humbert first showed the lath-like char-



Fig. 33. Putnam clay (heidelite), fraction 100-50 m $\mu$ . (Marshall *et al.*, 16.)

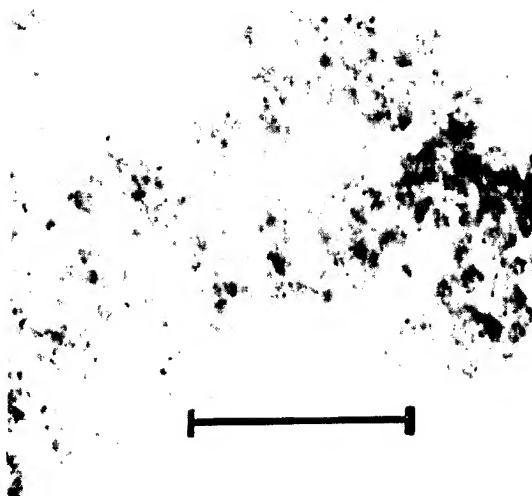


Fig. 34. Putnam clay (heidelite), fraction < 20 m $\mu$ . (Marshall *et al.*, 16.)

acter of this mineral for submicroscopic particles (19). The fraction 200–50  $m\mu$  is here illustrated (Marshall *et al.*, 16). Measurement of ten particles gave mean dimensions  $569 \times 108 m\mu$  and the thickness was roughly estimated at 14  $m\mu$ . Many particles show striations parallel to the length. In the finer fractions, the laths were somewhat shorter in proportion to their width.

*Hectorite (Magnesium Bentonite)* (Fig. 36). One fraction is here shown 500–200  $m\mu$ , (Marshall *et al.*, 16). It is clear that there is considerable aggregation in the coarser material. The individual laths are thin and striated and are somewhat longer in relation to their width than those of

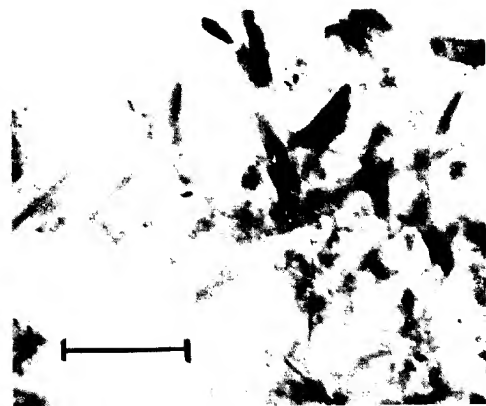


Fig. 35. Nonttronite, fraction 200–50  $m\mu$ . (Marshall *et al.*, 16.)

nonttronite. Ten particles of the 200–50  $m\mu$  fraction gave mean dimensions  $680 \times 67 m\mu$ . As the particles become smaller, their aggregates present a fluffy appearance.

*Montmorillonite* (Figs. 37 and 38). The German workers (1, 7) noted that the appearance in the electron microscope varies considerably according to locality and the fraction employed, some being exceedingly fluffy and ill-defined, while others consist of thin but clearly defined plates. In Fig. 37 we have the fluffy type (Wyoming bentonite, fraction < 200  $m\mu$ , Marshall and Dufford). Fig. 38 (Wyoming bentonite, fraction 2  $\mu$ –1  $\mu$ , Shaw, 20) illustrates the obviously platy type.

*Sauconite* (Fig. 39). This zinc clay resembles the platy montmorillonite rather than the lath-like hectorite. (Fraction < 1  $\mu$ , Marshall and Yudovitch.)

*Attapulgite* (Fig. 40). The fraction 500-200  $m\mu$ , is shown (Marshall *et al.*, 16). The individual fibers or rods are well defined and show considerable tendency toward parallel orientation. It is evident that some may have sedimented as bundles during fractionation. The presence of some isometric grains as impurity affords a satisfactory check on the settling



Fig. 36. Hectorite, fraction 500-20  $m\mu$ . (Marshall *et al.*, 16.)

velocities. In the fraction 200-50  $m\mu$ , ten particles gave mean dimensions  $685 \times 22 m\mu$ .

*Sepiolite* (*Meerschaum*) (Fig. 41). Highly asbestos-like. The habit is distinctly different from that of attapulgite, closely packed bundles of thin rods being rarely found.

In conclusion certain factors which may affect the electron micrographs of clay minerals should be mentioned, although relatively little systematic





Fig. 37. Montmorillonite. Fluffy type. (Wyoming Bentonite fraction  $\rightarrow 200 \text{ m}\mu$ .)  
(Marshall and Dufford — unpublished.)



Fig. 38. Montmorillonite. Platy type. (Wyoming Bentonite, fraction  $2\mu-1\mu$ .)  
(Shaw, 20.)

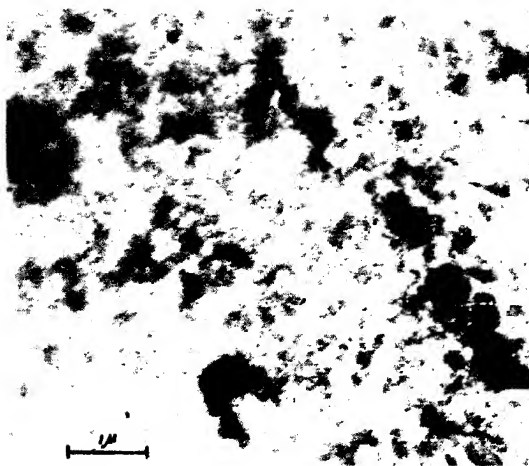


Fig. 39. Sauconite. (Marshall and Yudovitch—unpublished.)



Fig. 40. Attapulgite, fraction 500-200 mμ. (Marshall *et al.*, 16.)

investigation has been made. The first concerns the nature of the exchange cation. The alkali cations are known to favor maximum dispersion, whereas hydrogen and the alkaline earth cations may in some cases give similar particle sizes, in others may cause a partial oriented coagulation, and in still others may produce a random complete coagulation, depending upon the clay type and upon the concentration of the suspension. The nature of the liquid in which the clay is suspended is also of great impor-



Fig. 11. Sepiolite, Meerschaum. (Marshall and Dufford—unpublished.)

tance, as may readily be seen in Figs. 79 and 80, Chapter 14, which show electron micrographs of a montmorillonite prepared by Jackson in two different ways, one a sodium clay dried from water, the other a calcium clay dried from benzene.

A second factor to be considered is a possible coagulation of the clay particles during the evaporation of the drop of suspension upon the colloidal support. This is probably of small importance (except perhaps in the case of relatively concentrated systems of rod-shaped particles), provided the drying is of only a few seconds duration.

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## CHAPTER 8

### THE OPTICAL PROPERTIES OF CLAY AGGREGATES AND SUSPENSIONS

#### *Clay Aggregates*

The optical constants of the clay minerals can rarely be determined upon single crystals of microscopic size. Much of the primary data used for identification purposes relates to the properties of aggregates. However, since most of the aggregates are formed by a similar process of stacking plate-like units one upon another, this circumstance has caused less hindrance than might be supposed. In one case, aggregates have proved consistently misleading. Halloysite was, until the advent of the electron microscope, supposed to be platy, like kaolinite, and to have practically zero birefringence. We now know that the particles are elongated, and, by their electrical orientation in dilute suspensions, it has been shown that they possess an appreciable birefringence (14).

The form birefringence caused by the parallel arrangement of plates or of rods arises, as Wiener showed, whenever the ultimate units are separated by a medium of different refractive index (15). If solid and liquid have the same refractive index it vanishes. It attains a maximum value when the two phases are equal in volume. There are three reasons why this Wiener effect has proved of little importance in dealing with the clays. (1) In characterizing dried clay flakes the refractive indices parallel and at right angles to the plane of the flakes are determined by the immersion method and the birefringence is usually taken as the difference between them. Provided the liquid penetrates the aggregate the Wiener birefringence will be zero. (2) In some cases, notably where only slightly polar organic molecules are used, the liquid may not penetrate between the ultimate particle units. Hence, a Wiener effect would be expected. However, in the formation of clay flakes derived from minerals of the expanding lattice group, the particles pack so closely together that no clear distinction can be made between inter- and intraparticle spacings (1). The system can be regarded as comprising only a single optical phase and the Wiener effect is zero. The measured birefringence is then the same for the aggregate as for the single particle. (3) In measurements of the birefringence of dilute clay suspensions the possible contribution of the Wiener effect should not be overlooked. In certain cases examined by the author (fractions of Putnam clay) change of the refractive index of the liquid caused no appreciable

change in measured birefringence using electrical orientation (7). Hence, the Wiener effect was negligible.

The actual properties of dried clay flakes are in some respects different from those of idealized layers of plate-shaped particles. As was first demonstrated by Hendricks and Fry (5), many clay minerals give biaxial optical interference figures when viewed at right angles to the plane of the flakes. The optic axial angles are reproducible for a given pretreatment, but vary with the nature of the exchangeable base present. Such biaxial character-

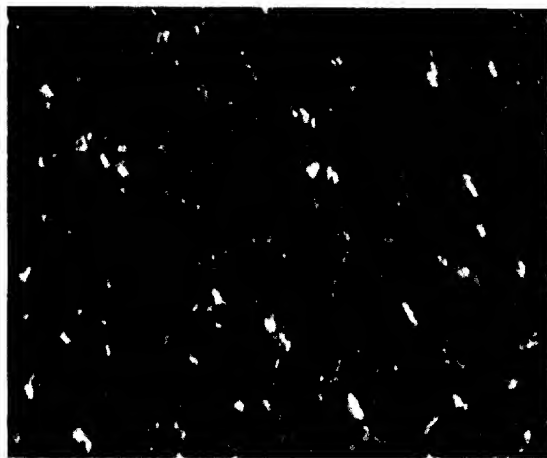


Fig. 42. Birefringence shown by a clay film produced by rapid evaporation. Photograph taken at 300 diameters under crossed nicols.

istics suggest some degree of orientation within the plane of the flakes. Smith (13) has shown that mechanical factors during drying are largely responsible for biaxial figures. The examination of very thin clay flakes in the polarizing microscope using high magnifications has shown that, on the micro scale, the optical properties vary considerably from place to place. Fig. 42, taken with crossed nicols, illustrates this. The light areas show considerable birefringence, but both the extinction positions and the apparent birefringence vary from place to place. If the specimen had conformed to the idealized model of uniform layers of parallel plates the effect under the polarizing microscope would have been a uniformly dark field. With slower rates of evaporation a more nearly uniform field is obtained.

### Orientation in Flowing Suspensions

The first demonstration that submicroscopic clay particles (kaolin clays) were crystalline was furnished by the Zocher method. Baehmann found that rotational flow produced a dark cross under crossed nicols (1). Flow through a tube also causes orientation, giving rise to a measurable birefringence (Bradfield and Zocher, 2; von Buzagh, 3). The exact manner of orientation of plate-shaped particles in flow through a tube was finally demonstrated by Langmuir (6). The plates are tilted toward the center

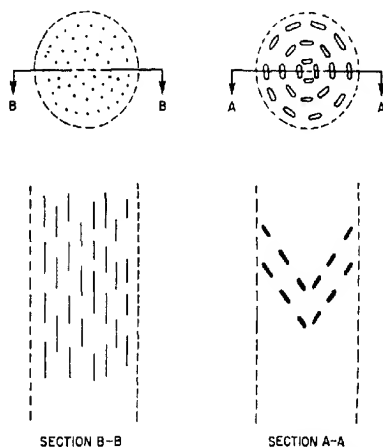


Fig. 43. Flow of suspensions of rods and plates through cylindrical tubes. In each case the vertical section gives only the orientation in the median plane. The complete figure would involve rotation of this plane through  $180^\circ$ .

of the tube in the direction of flow (Fig. 43). On observing with polarizer and analyzer, the extinction positions at the sides are equally inclined to that in the middle. Langmuir ascribed this to the interaction of the streamline flow upon long-range forces which tended to hold particles in certain equilibrium positions in the sol. This explanation would seem, however, to be inadequate where very dilute systems are concerned. The author (8) has shown that the effect persists unchanged down to very low concentrations. Here, purely hydrodynamic factors would greatly predominate over interparticle forces.

Alignment of rod- or plate-shaped particles by flow shows itself in two other ways. A beam of light entering the oriented sol will experience differ-



ent amounts of diffraction according to its direction. Light traveling perpendicular to the smallest dimension of the particles will be less diffracted than that perpendicular to the largest dimension. This is known as dityn dallism. Observations of this kind on clay minerals have been made by the author (8), but the results did not throw any very clear light on particle shape, owing probably to the tilting described above. The complementary absorption effect, known as conservative dichroism has not yet found application to the clays.

#### *Electrical Orientation in Clay Suspensions*

Before electrical orientation was applied to the clays, several researches on other systems had been published by Freundlich, Kruyt and their co-workers. Using particles of extreme shapes, such as the long needles of vanadium pentoxide sols, they showed that the electric field produced an orientation of the particles relative to the electrical lines of force. They ascribed this orientation chiefly to hydrodynamic causes. The electric current set the particles in motion by cataphoresis; these presumably then oriented themselves into positions of minimum hydrodynamic resistance. Hence, for the long  $V_2O_5$  needles the most natural orientation would be along the electrical lines of force, parallel to the direction of cataphoresis. Later, however, in an extremely illuminating but neglected paper, Procopiu (12) clearly demonstrated that, for various mineral suspensions, the prime cause of orientation was electrical rather than hydrodynamic. It was due to the electrical anisotropy of the particles themselves; that is, to the fact that, in all crystals except the cubic, there are different dielectric constants in different directions. Thus, irrespective of the shape or the hydrodynamic conditions of flow, a turning moment operates when an electric field is applied, until the direction of greatest dielectric constant becomes parallel to the lines of force. Marshall (7) was able to show that this mechanism greatly predominates over the hydrodynamic factors in the case of the clays. Quantitative measurements were undertaken under a variety of conditions. Thus it came about that three years before the structure of the swelling clays was elucidated by X-ray methods, the study of their birefringence in dilute suspension provided clear evidence on the following points. (a) The particles are crystalline, even down to the smallest sizes. (b) They possess an inherent anisotropy related to the base exchange properties. In other words, the sites of base exchange are not primarily external to the particles, but internal; not arranged at random, but in some definite pattern within the crystals. (c) Certain crystalline clays possess a marked property of oriented coagulation.

Some typical results on fractions of Putnam clay (beidellite) are given in Table X. At the voltage used, the saturation value had been reached in the case of the hydrogen and calcium clays, but not for the potassium

clays. Furthermore, the hydrogen and calcium clays were very similar in particle size throughout, whereas the potassium clays were much more highly dispersed and corresponded exactly to the limits given in the table. The calcium values are consistently higher than the hydrogen values. Since, therefore, cation exchange affects the birefringence, it is essentially an internal anisotropic property. No such variation is found in kaolinite. The potassium clay fractions of the Putnam clay show a decrease in birefringence with decreasing particle size. This is due to incomplete orientation; small particles require higher voltages for attainment of the saturation values. An ultramicroscopic study of these fractions showed that the potassium clay was much more highly dispersed than the hydrogen or calcium clay. The latter must, therefore, consist of compound particles made up of smaller ones in some oriented arrangement. That this orientation is a permanent feature, and not a transient effect brought about by the electric

TABLE X

Exchange cations	Birefringence (at 800 volts/cm. 60 cycles A.C.)		
	500 - 200 m $\mu$	200 - 100 m $\mu$	<100 m $\mu$
H	.023	.029	.026
Ca	.026	.031	.031
K	.023	.020	.011

current, is shown by the marked dityndallism and birefringence of the hydrogen and calcium clays in flow experiments.

Dilute bentonite sols (montmorillonite) showed some additional peculiarities. Oriented coagulation was absent in the dilute hydrogen and calcium systems. The lithium and sodium clays sometimes gave a negative instead of a positive birefringence. This change of sign had previously been observed in flow experiments (2) and was ascribed by the author to a change in the dimensions of the optical ellipsoid.

More recently Müller (9, 10) and Norton (11) have examined the effects of frequency variation upon the electrical birefringence of bentonite sols. At low frequencies negative values were found, changing to positive at high frequencies. The lower the concentration of the sol, the lower the range of frequencies for which negative values were observed. It was concluded that the negative values were due to the presence of long range interparticle forces, the positive ones being normal for an orientation like that of the Kerr effect. The Kerr constant of bentonite sols was calculated to be some  $10^6$  times that of nitrobenzene.

Thus, although certain complications are to be found in measurements of electrical birefringence, it can be used as a valuable tool in the characterization and identification of the clay minerals. Recent measurements by Whiteside and Marshall (14) have shown how high A. C. voltages serve to extend the range of the method. At 4000 volts/cm., with 60 cycle A. C.

current, the saturation values for Na and K clays can be attained. The results showed that, for the Putnam clay, these are very significantly lower in birefringence than is the hydrogen clay.

The presence of a strong positive electrical birefringence which is not appreciably affected by changes in concentration (that is, when calculated back to the solid basis), or changes in the refractive index of the liquid, may be interpreted as follows: The optical and electrical ellipsoids are similar in character. In the case of beidellite both have the greater axis in the plane of the plates. Since the particles in suspension are presumably free to rotate about the largest electrical axis, the measured birefringence would seem to be  $n_\gamma - \frac{n_\alpha + n_\beta}{2}$  which, when  $n_\beta = n_\gamma$ , becomes  $1/2(n_\gamma - n_\alpha)$ .

No quantitative measurements of diatrypsism or of conservative dichroism in electrically oriented clay suspensions have been published. Orientation by intense magnetic fields does not appear to have been investigated.

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## CHAPTER 9

### ADSORPTION BY THE CLAYS AND ITS CONSEQUENCES

#### *The Uptake of Nonpolar Molecules*

The clays have long been known to act as adsorbents, although their capacity for the uptake of nonpolar molecules is lower than that of the best activated charcoal or silica gel. Inert gases are taken up at low temperatures. In this way an estimate of surface area can be made (Brunauer, Emmett and Teller Method). By applying this technique to various clay minerals, Nelson and Hendricks (32) have shown that the surface areas deduced from the measurements correspond to external surfaces. The enormous internal surface of clays of the montmorillonite group does not come into play. The conditions of the experiment are such that measurements are made on dehydrated materials—that is, the  $c$  axis spacing is at a minimum. It would indeed be surprising if, under these conditions, molecules of inert gases should force themselves between the lattice units.

Little quantitative information is available regarding the adsorption of nonpolar vapors at ordinary temperatures. Benzene and carbon tetrachloride do not cause swelling or increase in the  $c$  axis spacing of the montmorillonite clays (18, 19). No measurements on attapulgite or sepiolite are available. These, with their spacings of fixed width might, be expected to show considerable internal adsorption for molecules of the right size, that is, with cross sections less than  $6 \text{ \AA} \times 3.8 \text{ \AA}$ .

#### *The Uptake of Polar Molecules*

The strong affinity of the swelling clays for water, first received a structural interpretation in 1933, when Hofmann, Endell and Wilm showed that uptake of water vapor by montmorillonite caused an increase in the  $c$  axis spacing but no appreciable change in the  $a$  or  $b$  axes (17). Shortly afterwards other polar liquids were shown to exert the same effect (18). The montmorillonite group is, in this respect, unique in mineralogy. It is not surprising, therefore, that many workers have since attempted to define with greater precision the exact role of the polar molecules. Their results are in general qualitative agreement but differ in their quantitative aspects, due probably to differences in the clays themselves as regards lattice composition, and as regards exchange cations.

Four sets of results are of special importance in discussing the role of water molecules. In 1936 Nagelschmidt (31) and Hofmann and Bilke (19) published curves showing the relationship of  $c$  axis spacing to water con-

tent and to vapor pressure. In both cases somewhat *S-shaped* curves were found (Fig. 44), characterized by a rapid increase in the *c* axis spacing for the first additions of water vapor, followed by a region where water was taken up with smaller increase in the spacing. Finally, at high vapor pressures, the curve again became steeper. Nagelschmidt showed that, in the initial rapid increase, the expansion was greater than that corresponding to the volume of the water molecules. He supposed that the water entered at first between the silicate sheets but was later adsorbed on external sur-

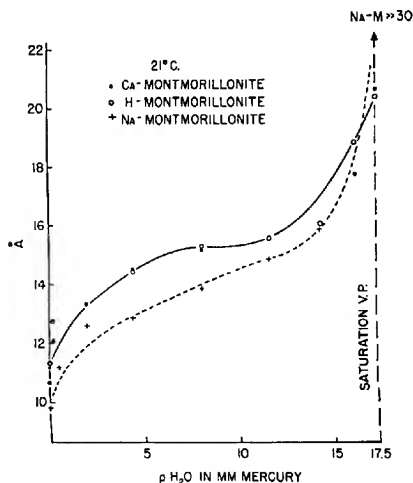


Fig. 44. Variation of the C axis spacing of montmorillonite with change in the aqueous vapor pressure. (Hofmann and Bilke.)

faces as the vapor pressure increased. As pointed out by the author (30), it seems more likely that the first water molecules congregate around the exchangeable cation sites between the sheets. Then, later additions fill up the vacant spaces, and finally, again force the layers apart at high vapor pressures. A close association of the water molecules with the exchange cations is not unreasonable in view of Taylor's similar conclusion for the zeolites. On the other hand, Bradley, Grim and Clark (5), working with hydrogen bentonite, have postulated the existence of distinct hydrates and their mixtures to explain the X-ray results. The first layer of water molecules, corresponding to 6  $\text{H}_2\text{O}$  per unit cell, occupies a vertical height

of 2.8 Å; the later additions of units of 6 H<sub>2</sub>O, up to 24 H<sub>2</sub>O add 3.0 Å in height per layer. The influence of the exchange cation upon the condition of the water has been traced in some detail by Hendricks, Nelson and Alexander (14). Montmorillonites saturated with H, Li, Na, K, Cs, and with Mg, Ca, Sr, and Ba were employed. Thermal analysis curves were combined with the X-ray data. In this way it was shown that the low temperature (200°C.) peaks in the thermal analyses are affected by several components. For the calcium and magnesium clays two of these could be rather clearly distinguished, since their maxima were separated by a sufficient temperature interval. The one corresponding to the higher temperature became more prominent at low relative humidities. The amount of water associated with this component was approximately sufficient to provide 6 H<sub>2</sub>O for each Ca or Mg ion. This was about half the quantity needed for completion of a single layer of water molecules. Still further additions caused completion of the first layer and, finally, second and third layers were formed. By a comparison of the intensities of the X-ray lines corresponding to the *c* spacing with the thermal data, it was shown that in many cases only a part of the material actually has the determined *c* axis spacing, the rest being in some unordered distribution of spacings. This helps to explain the great variation in relative intensities found by different workers. It seems that, in general, the montmorillonite clays are characterized by a distribution of *c* axis spacings which may either be almost completely random (certain beidellites) or almost completely uniform, depending upon the atomic replacements in the clay structure, the exchangeable cations, the relative vapor pressure, and the previous history of the sample.

From the data of Hendricks, Nelson and Alexander the moisture contents per gram of montmorillonite when saturated with different cations may be compared (Table XI). The influence of the hydration of the cation is strongly seen, especially at the lowest humidity.

Evidence on the condition of the water in montmorillonite clays has also been obtained by Buswell and Dudenbostel (6) using infrared absorption spectra. Two peaks in the absorption spectra, at 2.75 μ and 2.92 μ, respectively, were found to vary in height with the hydration. The peak at 2.75 μ was ascribed to "free OH"; that at 2.9-3.0 μ to "hydrogen-bonded OH." The variation in the latter was strongly marked. Thus, Ca and Mg clays showed by far the greatest absorption at 2.92 μ, then Ba, Li and K clays followed, then H clay, then Na clay, and, least of all, NH<sub>4</sub> clay. These figures are not in the usual order of hydration of cations. It must be remembered, however, that the measurements are made upon thin films of dried clay subsequently brought to various humidities. The total moisture content of the films was not determined, and the assumption that it was pro-

portional to areas under the curves may not be entirely justified. Evidently, also, fixation effects and the factors affecting film structure will have influenced the results. In general, this investigation strongly reinforces the views held by Taylor, and by Hendricks and Jefferson, on the arrangement of water molecules in silicate structures.

The particular configuration of water molecules which form a single molecular layer is not known with any certainty and, indeed, all variations from planar randomness to the hexagonal arrangement suggested by Hendricks and Jefferson (13) may perhaps exist, depending upon the exchangeable cations, total water content, and temperature. Hydrogen montmorillonite apparently shows the greatest orderliness in this respect. Hendricks has suggested that the water molecules of the first layer form hydrogen bonds

TABLE XI  
*Moisture Content of Mississippi Bentonite when Saturated with Different Cations*  
(Results in g. H<sub>2</sub>O /g. dry clay)

Cation on clay	Relative humidity		
	5%	40%	90%
H	.045	.165	.36
Li	.065	.155	.34
Na	.025	.105	.28
K	.015	.080	.20
Cs	.020	.080	.18
Mg	.085	.195	.34
Ca	.070	.200	.36
Sr	.050	.200	.34
Ba	.050	.140	.32

with the appropriate oxygen atoms of the silica sheet, the arrangement being such that each oxygen atom of the water is tetrahedrally surrounded by four hydrogens. This suggestion derives its chief strength from X-ray work on endellite and vermiculite and the analogy with the zeolites (see Figure 21, Chapter 5).

The sorption of ammonia by hydrogen montmorillonite has been studied by Cornet (7). Several processes merge into one another. At the lowest pressures, ammonia gas is absorbed with no change in the *c* axis spacing. Apparently it is taken up first on the outer surfaces, then internally by direct reaction with the exchangeable hydrogen, thus becoming exchangeable ammonium. Later, the ammonia shows its strongly polar character by forcing the layers of the lattice apart. The ammonia first added, that is, the exchangeable ammonium, is driven off last in thermal decomposition experiments.

Polar organic molecules, such as alcohols, ketones, *etc.*, were shown by Hofmann *et al.* (18) to cause increases in the *c* axis spacing of montmorillo-

nite. A more detailed X-ray study has been made by Bradley (4). Ethyl alcohol and a number of glycols and glycol ethers were found to give well defined double molecular layers between the silicate units and were strongly adsorbed. The energies involved are apparently greater than for water, since clays dehydrated at 400–500°C. lose their capacity for swelling in water but swell with glycols or amines.

All members of the montmorillonite group were shown by Bradley to give a double molecular sheet with ethylene glycol, the characteristic spacing being 17 Å. Halloysite, in the fully hydrated form (endellite), also took up ethylene glycol to give a single molecular layer, half the water remaining. This observation confirms Hendrick's structure for endellite, in which kaolinite units alternate with double layers of water molecules. In the vermiculites, and in attapulgite, little uptake of ethylene glycol occurred.

MacEwan (26, 27) pointed out the usefulness of ethylene glycol in identifying montmorillonites and has also shown that it is taken up by halloysite (27) even after the latter has been gently dehydrated. It is thus possible to pass back from metahalloysite to endellite through the glycol compound, provided the metahalloysite has been produced at a low temperature.

Much interest has centered around the sorption of organic bases and their salts. Giesekeing (11) showed that montmorillonites in which large organic cations were present as exchangeable bases had lost the power of swelling in water. At the same time the *c* axis spacing became better defined, as shown by the greater intensity of the corresponding line in the X-ray pattern. Large organic cations could be replaced by others of similar size but small inorganic cations had little effect in displacement. The proteins (8, 9) are taken up as cations on the acid side of the isoelectric point. The exchange capacity for small inorganic cations is thereby reduced and *c* axis spacings as high as 48 Å (using casein) may be imposed upon the clay structure. Hendricks (16) has also investigated a group of organic bases with particular reference to the orientation of the molecules adsorbed between the sheets. He showed that strong van der Waals forces come into play, in addition to the electrical attraction of the organic cation for the negatively charged silicate surface. These showed themselves in two ways. First, the organic cations were constrained to take up, as far as possible, a planar configuration parallel to the silicate layers. Second, in such arrangements numerous exchange spots were made inaccessible for reaction and the total exchange capacity decreased.

Several publications have dealt with the brilliant colors produced when clays, especially those of the montmorillonite group, are brought into contact with certain aromatic amines or their derivatives (3, 10, 12, 15, 33). The mechanism of this reaction and its possible use as a test for mont-



morillonite clays have been debated. All authors agree that the colored compounds are of the semiquinone type, which normally arises by gentle oxidation of the appropriate amine. It is established that the colored compounds cannot be extracted by solvents from their association with the clays. Where the clays contain demonstrable amounts of oxidizing agents, such as ferric ions, the colored compounds are readily produced. Clays which have been acted upon by powerful reducing agents do not show the test.

#### *Heat of Adsorption*

Although no measurements are available on the differential heats of adsorption of pure clay minerals, a number of determinations of the integral heats of wetting are found scattered in the literature. Most of these were made by soil scientists interested in the relationship of the different colloidal properties with one another. In few cases were the clays employed properly characterized in a mineralogical sense. Nevertheless, some significant results have been obtained.

As would be expected, the heat of wetting is much greater for polar liquids like water, than for relatively inert ones like carbon tetrachloride. No quantitative relation between the physical properties of the liquid molecules and the heat of adsorption has yet been found. Fig. 45 illustrates the difference between water and carbon tetrachloride, using data of Janert (21) for a "brick clay."

Using a variety of clays prepared from soils, Anderson and Mattson (1) and Baver (2) found that a linear relationship between the heat of wetting and the base exchange capacity could be traced over a considerable range. However, experiments on pure clay minerals are not available, so that it is impossible to say anything definite about the heats of adsorption in relation to surface structure. Janert has shown that the heat of wetting varies with the nature of the exchange cation in the order  $\text{Ca} > \text{Mg} > \text{H} > \text{Na} > \text{K}$ , whereas the calculated heats of hydration for dilute aqueous solutions give the series  $\text{H} > \text{Mg} > \text{Ca} > \text{Na} > \text{K}$ . The heats of wetting, calculated per cation equivalent, are only a fraction of the heats of hydration. In the case of hydrogen the fraction is  $1/12$ , as against  $1/9$  for magnesium,  $1/7$  for calcium, and  $1/5$  for sodium and potassium. It must be remembered, however, that the later additions of water are probably not closely associated with exchange cations and clearer evidence would probably be afforded by measurements of the heat evolved for limited hydration. The limited dissociation of the clays is also qualitatively reflected in these figures.

The method devised by Harkins for the determination of total surface

area by a heat of wetting determination at 100% humidity has not been applied as yet to the clays. It is practically certain that the swelling clays would not lend themselves to this type of experiment owing to the practical impossibility of bringing them to a true equilibrium with water vapor at 100% humidity in any reasonable length of time. In the case of nonswelling clays, such as kaolinite, there are better prospects, but the presence of capillary condensation might still invalidate the results.

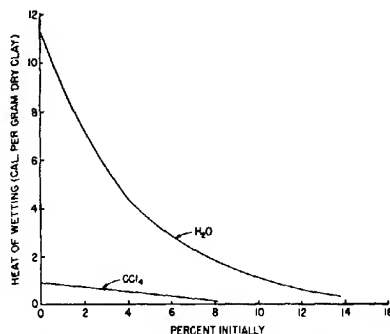


Fig. 45. Data of Janert on heat of wetting.

#### *The Significance of Experiments on the Fine Grinding of Clay Minerals*

In 1931 appeared a paper by Kelley, Dore and Brown (22), which contained the new observation that the base exchange capacity of certain clays could be increased by dry grinding in a ball mill. In this process, previously nonexchangeable cations became exchangeable. The conclusion drawn, natural enough at the time, was that fine grinding, by exposing new surfaces, made accessible, and therefore exchangeable, cations which had previously formed part of the internal structure. This work was further elaborated and developed in two papers published in 1936 (23, 24). It was pointed out that an increase in the water retained at a given temperature and a change in the general shape of the dehydration curve accompanied the increase in exchange capacity. These results were interpreted as follows: The total surface could be increased in two ways, either by cleavage parallel to the plane of the plates or by fracture at right angles. Corresponding to the former there would be an increase in the rather loosely held "planar" water adsorbed upon the flat surfaces. Fracture of the plates, on the other hand, would lead to an increase in "broken bond" water which was more tenaciously held. The increase in exchange capacity was ascribed

purely to the enhanced accessibility of cations (including H and Al) accompanying this increase in specific surface.

Prior to 1936, however, certain evidence not in agreement with these views had been presented. The original authors, in 1931, had pointed out that fine grinding in some measure destroys the crystalline structure, since it caused not merely a broadening of the X-ray lines, but an overall fogging characteristic of amorphous material. It was also shown by the present author, in 1935 (28), that for unground montmorillonite and beidellite the base exchange capacity increased very little with decreasing particle size. A further examination of the properties of the ground product from Putnam clay (beidellite) showed that it differed from the unground clay in the following ways: the ground clay had a low refractive index and showed little electrical birefringence in suspension; it was decomposed by dilute acetic acid, whereas the original clay was not (29). The author therefore suggested that fine grinding effectively destroys the original lattice and produces amorphous material having very similar properties to the permutites.

This interpretation was supported by the work of Jackson and Truog (20), who found similar effects when clays and other minerals were ground in a ball mill in presence of benzene or of water. A detailed investigation by Laws and Page (25) of the fine grinding of kaolinite has further shown that the ground product should be regarded as permutite-like.

Taken as a whole, therefore, this work points to a new field in colloid chemistry, the breakdown of silicate structures and their recombination to form new amorphous products by mechanical means. The process evidently involves atomic rearrangements, not merely comminution of particles and increase in specific surface. The constitution and properties of the amorphous products are quite distinct from those of the original minerals. Thus, few conclusions regarding the constitution of the clays can legitimately be drawn from experiments on the ground products.

In some cases deliberate attempts have been made to increase the specific surface of clays by fine grinding, without regard being paid to these changes. Misleading conclusions have naturally arisen. Thus, Stout's work (34) on the adsorption of phosphate by kaolinite was partially vitiated by his primary assumption that ground kaolinite was the same mineralogically as the unground clay.

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## CHAPTER 10

### CLAY ACIDS AND THEIR TITRATION CURVES

The application to the clays of Pauli's technique of purification by electro-dialysis was accomplished by Mattson (19) and Bradfield (6), and has been of immense importance. It has provided a basis for the electrochemical characterization of the clay minerals, in spite of the fact that complicating circumstances are present. These arise from the instability of certain clay minerals in acid solution. All gradations are found, from clays such as magnesium bentonite (hectorite) which decomposes completely on electro-dialysis leaving a silicic acid residue, to kaolinite which is relatively stable.

The process of electro-dialysis does not consist simply of a removal of mobile cations to the cathode chamber and of mobile anions to the anode chamber, although this predominates in the first stages. Basic constituents, such as iron and magnesium, are frequently found at the anode while silicic acid moves in considerable quantities with the bulk of the bases to the cathode (8). Johnson and Norton (10, 11) have emphasized that, even in the case of kaolinite clays, removal of adsorbed impurities can only be completely effected by several repetitions of electro-dialysis and neutralization with a soluble base.

The theoretical treatment of colloidal acids by Pauli and Valko (26) cannot be applied in any quantitative way to the clays, although the central concept of a series of dissociation constants of diminishing magnitude has relevance. The reason is that several additional complications arise. Many clay acids, as will be shown later, are in reality not purely hydrogen systems but possess a mixed character in which exchangeable aluminum plays an important part at low pH values. Secondly, the clay salts are only partially ionized in solution, the degree of ionization varying with the base used and the extent of neutralization. Lastly, in strongly alkaline solutions certain clay salts decompose to some extent, giving aluminates and silicates which may be soluble or insoluble, depending upon the base (7). Kaolinite is less affected by these disturbing factors than are the expanding lattice clays. In general, therefore, clay acids cannot be quantitatively compared with soluble acids nor with simple colloidal electrolytes like agar. When such comparisons are attempted, contradictory conclusions emerge. Thus, one experiment will seem to indicate that a particular clay is a very weak acid while another points to an acid of considerable strength.

#### *Effect of Concentration and of Particle Size*

The work of Bradfield (3, 4, 5), and of Wiegner and Pallmann (25, 28), established the fact that the acidity of clays is not due to substances in true

solution. For colloidal acids generally, the term "suspension effect" was introduced by Wiegner and Pallmann. This term expresses the fact that the hydrogen ions accompany the colloidal particles. Thus, when a highly purified acidic colloidal system is centrifuged until complete separation is achieved, the supernatant liquid has no acidity and the concentrated colloid has all the acidity of the original system. This can be shown in various ways; by pH measurements, by reactions depending on the presence of hydrogen ions, such as the inversion of cane sugar or the color change of indicators, and by titration. The acid suspension effect persists up to that pH where the titration curves for different concentrations cross. Beyond this the effect is inverted, that is, the higher concentration corresponds to

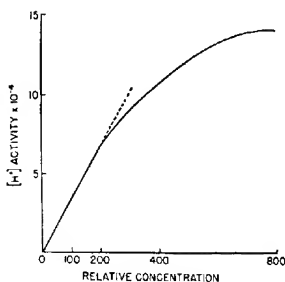


Fig. 46. Hydrogen ion activity in relation to clay concentration. (Wiegner and Pallmann.)

the lower hydrogen ion concentration. This was termed the alkaline suspension effect by Wiegner and Pallmann.

At low concentrations of clay there is a linear relationship between the concentration of clay and the hydrogen ion activity as calculated from pH measurements (25, 28). This bends around at higher concentrations (Fig. 46). Hauser and Reed (9), working with monodisperse fractions of hydrogen bentonite, found that, on plotting the logarithm of the concentration against the pH, a single straight line resulted, irrespective of particle size (Fig. 47). This important observation is in complete harmony with our present views on the structure of the expanding lattice clays. All parts of the system, including the interior of the larger particles, are accessible to small exchangeable cations. The pH measurement expresses the mean electrochemical work which must be done in the imaginary transfer of a small fraction of the hydrogen ions from the sol to an arbitrary standard solution. All parts of the sol system can, therefore, contribute to this value. We can

imagine a single particle to be surrounded by a series of concentric layers or shells. In the outermost the activity coefficient of the cation is 1; as we approach the particle surface the coefficient diminishes. The experimental result indicates that the average contribution of each unit cell surface to the total hydrogen ion activity is practically independent of its position. Whether it faces the intermicellar liquid, or another aluminosilicate unit at say 20–30 Å, appears to make no difference, at least in the case of the acid montmorillonite studied by Hauser and Reed. This, of course, may not always obtain.

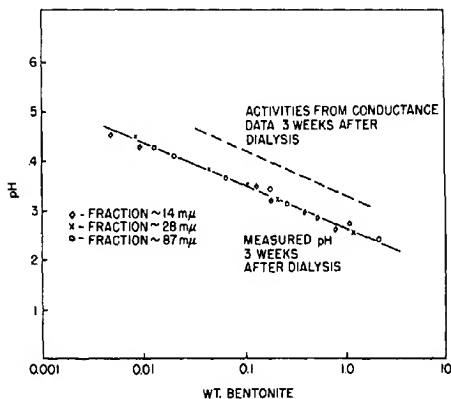


Fig. 47. Linear relationship between pH and log (clay concentration) for hydrogen bentonite fractions. (Hauser and Reed.)

We shall see later that, with larger cations, especially calcium, certain peculiarities of the titration curves can be explained by assuming a distinction between cations forming the outer atmosphere and those which enter between the lattice units. Even the monovalent cations sodium, potassium, and ammonium display such differences, though over a much narrower range than calcium. The result with hydrogen ions may be due partly to the fact that the electrodyalyzed clays studied were actually hydrogen-aluminum systems, partly to the small size of the hydrogen ion in comparison with the distance of separation of adjacent lattice units.

In addition to pH measurements, conductivity determinations have also been made upon hydrogen clays. It is then possible to make a comparison between the measured conductivity and the contribution calculated for the hydrogen ions whose activities have been measured. In a number



of cases it has been found that the conductivity ascribed to the hydrogen ions alone is greater than the measured conductivity of the system. Hauser and Reed (9), Mitra (21), and Marshall and Krinbill (15), have all found this to be the case for montmorillonite. It is true also for illite (15) and for Putnam clay (beidellite) when freshly electrodialed (2), but not for kaolinite (21, 15). Partial or complete neutralization of the clay by bases, or a rise in pH on standing after electroanalysis restores the "normal" condition of affairs in which the conductance ascribed to the cations is a major fraction of the total conductance. Table XII, which includes some hitherto unpublished and some recalculated results, illustrates these relationships for four clay minerals.

TABLE XII  
*Potentiometric and Conductometric Data on Clay Acids*

Mineral	Concentration per cent	$a_H$	Conductance for $a_H$	Measured conductance
Montmorillonite ( $<200 \text{ m}\mu$ )	2.8	$1.48 \times 10^{-3}$	$5.15 \times 10^{-4}$	$4.15 \times 10^{-4}$
Beidellite <sup>a</sup> ( $<600 \text{ m}\mu$ )	2.35	$2.46 \times 10^{-4}$	$8.55 \times 10^{-5}$	$5.00 \times 10^{-5}$
Illite ( $<2\mu$ )	10	$3.2 \times 10^{-4}$	$11.3 \times 10^{-5}$	$7.68 \times 10^{-5}$
Kaolinite ( $<2\mu$ )	10	$2.4 \times 10^{-5}$	$8.3 \times 10^{-6}$	$1.13 \times 10^{-5}$

<sup>a</sup> These results are recalculated from Bayer's figures (2).

This phenomenon is not confined to montmorillonite, beidellite, and illite, but has been demonstrated also for electrodialed sols of gum arabic, starch, and tungstic oxide. Pauli and Valko (26) state generally that, in highly purified colloidal systems, the measured conductance is less than would be anticipated from that of the free ions plus that of the ionic micelles. However, no adequate theory has yet been presented. The experiments of Hauser and Reed (9), using bentonite carefully fractionated according to particle size, show certain features not previously demonstrated. In Fig. 48, taken from their paper, the specific conductance is plotted against concentration of clay for four fractions whose mean particle sizes were: No. 1,  $14.3 \text{ m}\mu$ ; No. 2,  $20.3 \text{ m}\mu$ ; No. 4,  $33.8 \text{ m}\mu$ ; No. 6,  $87.0 \text{ m}\mu$ . The broken line to the left gives the computed conductance ascribed to the hydrogen for all fractions (the activity measurements all fell on a single line). It is clearly apparent that the discrepancy is of major proportions and that it becomes greater as the particle size increases. The authors suggest that the larger particles, having greater negative charge, hold the hydrogen ions more tightly, but this is scarcely acceptable since it would

postulate that the particles act as point charges. The charge per unit surface, which is the more important quantity, would seem to vary little with particle size in these systems.

Qualitatively at least, a theory based on electrostatic shielding offers attractive possibilities. Consider a colloidal particle with its atmosphere of ions. The latter can be subdivided into a series of closed shells in which the ionic density decreases as their distance from the particle increases. Imagine now that everything within a certain shell is removed and replaced by pure solvent plus a single ion. On application of an external electric field, the single ion will be, to a certain extent, electrostatically shielded by the con-

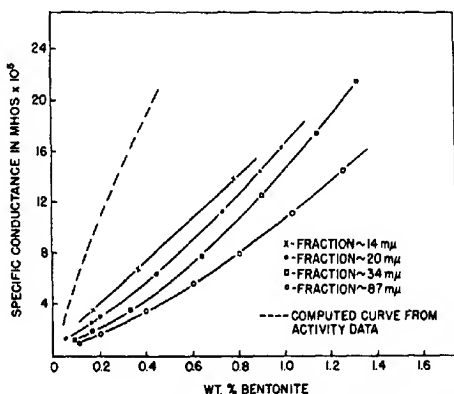


Fig. 48. Relationship between specific conductance and clay concentration for various hydrogen bentonite fractions. (Hauser and Reed.)

ducting shell around it. In other words, it will behave as if in the presence of a field of reduced magnitude. Extending this idea to the whole ionic atmosphere we can see that, as regards an external field, all ions except the outermost will have a reduced conductivity, the effect becoming greater as the particle surface is approached. The reduction will be greatest for the particle itself. Considering now particles of different sizes, but with the same surface density of charge, more conducting material will be retarded by this effect in the case of large particles than for an equal amount dispersed to smaller sizes. In other words, the more nearly the material approaches the molecular condition the smaller will this retardation become. However, even for true solutions it is not negligible, as the theory of Debye and Hückel shows.

We may conclude from this brief examination that the effect is general in colloidal systems. Their conductivities are less than would be anticipated from the sum of the contributions of atmosphere ions and charged particles considered separately. Colloidal acids show the effect through the normally highly conducting hydrogen ion, so that in many cases the conductivity ascribed to the dissociated hydrogen ions (measured potentiometrically) is greater than the actual conductivity of the whole system. It is clear also that substances showing internal conductance, like the montmorillonite clays, will display the effect more strongly than colloidal systems whose particles are electric insulators. Similarly, particles with a high surface density of charge will show it more than those with a low one.

In discussing the conductivity of clay sols, one qualitative observation first noted by Bradfield (7) is particularly enlightening. If, during electro-dialysis, a continuous plug or structure is allowed to form between the cathode and anode membranes, a relatively large current will pass. Then, if the structure is broken up, the current falls to a much smaller value, yet the total amount of material between the electrodes remains the same. The particles, when in contact, produce a continuous conductor. This effect is strongly shown by montmorillonite and beidellite, but has not been observed with the other clays, although it may perhaps exist to a minor degree. It may be ascribed to the interpenetration of the diffuse double layers, strongly aided by the fact that, once this interpenetration is achieved, the interior of the particles can also assist in the conductance. In this way conducting bridges are established across the whole system.

#### *Exchangeable Aluminum in Clay Acids.*

The most extensive investigations on well defined clay minerals, which deal with the entry and release of aluminum, were carried out by Paver and Marshall (27). They were designed to clarify earlier experiments by numerous soils workers, notable among whom was H. Kappen, whose results with zeolites have already been mentioned. Considerable light was thrown on the peculiar position of aluminum among exchange cations in the case of montmorillonite (Wyoming bentonite) and beidellite (Putnam clay). The salient features are as follows: (1) Unlike other trivalent cations, aluminum does not enter appreciably into electro-dialyzed clays by exchange; (2) Electro-dialyzed clays on treatment with neutral salts liberate aluminum. The amount increases with the concentration of the salt to a maximum which is approximately equivalent to the exchange capacity of the clay. Both hydrogen and aluminum ions are released in such experiments; (3) Neutral salt treatments liberate more aluminum than strong acids used at the same concentrations; (4) In a series of alternate neutral salt treatments followed by acid washings, aluminum is liberated chiefly

in the neutral salt treatments; (5) After a few repetitions, the release of aluminum ceases or falls to a very small amount.

It was concluded that these facts are best explained by the supposition that the clay acids of montmorillonite and beidellite are in reality hydrogen-aluminum systems. The aluminum arises by decomposition of parts of the clay lattice due to progressive attack by hydrogen ions. It was suggested that the chief action was breakage of Al-O-Si linkages. The possibility of the ionized Al arising by interaction of the clay acid with aluminum hydroxide impurity was experimentally excluded. Later work (1, 21, 23, 24) has confirmed these facts and has lent further support to the conclusions.

In particular, the Indian soil scientists have studied in detail the changes which occur when clays and soils undergo repeated desaturation and treatment with barium chloride. They worked with clays derived from Indian soils on which electrometric studies were concurrently being made (23). Finally the work was extended to include three well-defined minerals: montmorillonite, kaolinite, and pyrophyllite (24). With the first, the conclusions of Paver and Marshall were substantiated. Repeated cycles of desaturation and neutral salt treatment caused a steady decrease in the Al and a smaller decrease in the hydrogen released by exchange. Finally, after four treatments the ratio hydrogen released/aluminum released became very large. Successive treatments caused a large reduction in the exchange capacity of the montmorillonite, indicating considerable decomposition, which was confirmed by the appearance of soluble silica in the earlier desaturations. With kaolinite, aluminum and hydrogen were similarly brought into solution in the neutral salt treatments but their release caused no measurable reduction in the base exchange capacity and no soluble silica was found. Evidently, the attack on kaolinite is confined to external surfaces. With pyrophyllite the results were intermediate; a small amount of decomposition appeared to accompany the cycles of desaturation and neutral salt treatment.

#### *The Titration Curves of the Clay Acids*

Although there is ample evidence that clay acids cannot be treated simply as compounds having one or more clearly defined dissociation constants, no theory adequate to explain all their complexities has yet been found. Potentiometric and conductometric titration curves have been obtained in abundance, but their interpretation is still uncertain, as Mitra's excellent discussion shows (21). New experimental weapons in the shape of membrane electrodes sensitive to a variety of cations, are now available. With these we can trace the fate of the cation of the base used for the titration as well as the disappearance of the hydrogen. Information of this kind has been obtained by the author and his associates for montmorillonite, beidellite,

illite, and kaolinite in conjunction with potassium (13), ammonium (14), sodium (15), and calcium hydroxides (16, 18), and for nontronite and attapulgite with potassium hydroxide (8).

*Potentiometric Titrations.* The shape of the pH titration curves varies with the nature of the clay, its concentration, and with the base used; a large difference being apparent between mono- and divalent bases. In most cases, a single inflection point corresponds to what is commonly regarded as the point of equivalence. Its position varies with the base used and with

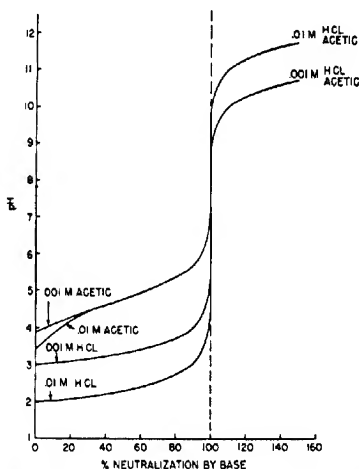


Fig. 49. Titration curves for 0.01 *M* and 0.001 *M* hydrochloric acid and acetic acid with a strong base.

the clay mineral. Double inflections have been reported for kaolinites by the Indian workers, and for a bentonite by Bradfield (7).

When different concentrations of the same clay are titrated with the same base, the pH curves often intersect at, or very close to, a common inflection point. This is true for beidellite, illite, and kaolinite according to the author's results (15). Montmorillonite, when investigated over a sufficiently wide range of concentrations, shows some variation of the inflection point in the sense that the higher the clay concentration the greater is the amount of base required per unit quantity of clay and the higher is the pH. This can be seen in the author's results with Wyoming bentonite, but is

more marked in a bentonite reported on by Mukherjee and Mitra (22). Some typical curves are presented in Figs. 50-53.

For comparison, Fig. 49 shows the situation with a soluble weak acid—acetic. Below the point of equivalence, the curve for acetic acid—sodium acetate mixtures is independent of the absolute concentration over a considerable range, since it may be sufficiently accurately described by the

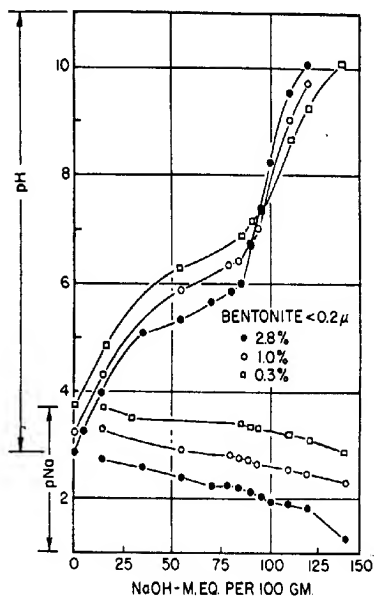


Fig. 50. pH (upper) and pNa (lower) titration curves for H-montmorillonite (Wyoming bentonite) with NaOH.

familiar equation  $\text{pH} = \text{pK} + \log (\text{salt}/\text{acid})$ . Thus the fact that very distinct curves are obtained for different clay concentrations shows how great is the divergence from the behavior of a soluble weak acid. Beyond the inflection point, the clay curves again diverge, but in the opposite order. This, however, would also be found with different concentrations of acetic acid or of a strong acid using this method of plotting. If now, we compare qualitatively throughout with what would be expected of a strong soluble acid, the divergence of the curves at low pH values is in agreement. For mont-

morillonite and beidellite we find that, for a concentration ratio of 10:1, the distance apart of the two curves corresponds to a pH difference of almost exactly 1 unit from say 40–70% neutralization. This difference is characteristic of strong acids, as may readily be seen by drawing the curves for  $N/100$  and  $N/1000$  HCl and comparing them with the single curve given by acetic acid (Fig. 49).

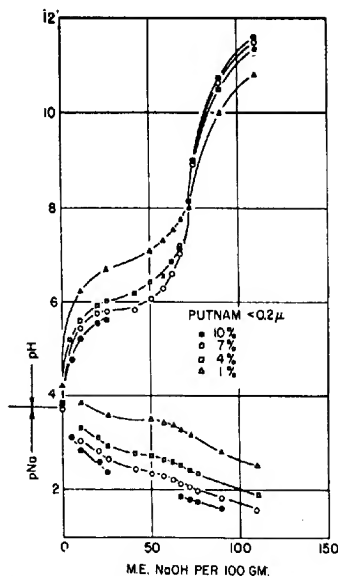


Fig. 51. pH (upper) and pNa (lower) titration curves for H-beidellite (Putnam clay) with NaOH.

The behavior of kaolinite is much closer to that of a soluble weak acid. Over a considerable range on the acid side of the point of equivalence, the titration curves for 10% and 1% suspensions run only 0.2–0.3 pH units apart, compared with 0.7 units for illite and 0.9–1.1 units for beidellite and montmorillonite.

Below about 30% neutralization the pH curves generally approach each other more closely, and the free clay acids give pH values which are related to concentration in much the same way as those of soluble weak acids. This

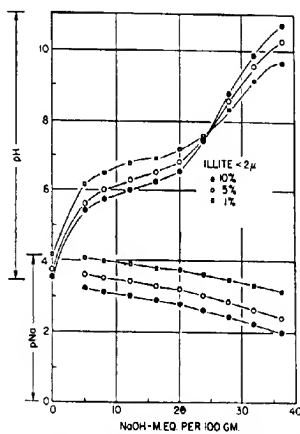


Fig. 52. pH (upper) and pNa (lower) titration curves for H-illite (Grundite) with NaOH.

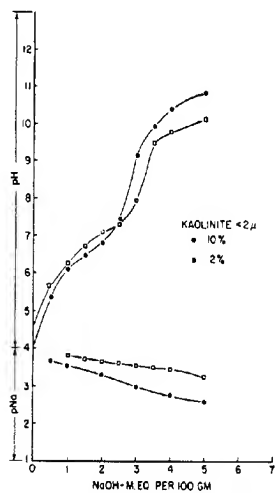


Fig. 53. pH (upper) and pNa (lower) titration curves for H-kaolinite with NaOH.



fact, however, may be deceptive. The real strength of montmorillonite and illite as acids is certainly masked by attack upon the exposed parts of the lattice by hydrogen ions. This results in the formation of ionized aluminum, the clay acid thus being essentially a hydrogen-aluminum clay.

The pH titration curves of the clays with strong monovalent bases thus display different characteristics in different parts. The initial steep portion appears characteristic of a weak acid; then the decrease in slope and the divergence at different concentrations show a more strongly acid character; finally, the slope near the point of equivalence is more nearly characteristic of a weak acid titrated with a weak base.

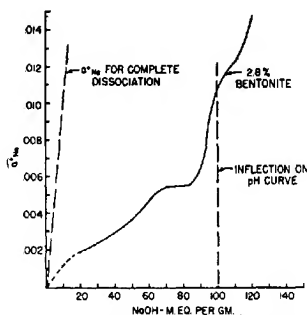


Fig. 54. Sodium ion activity plotted against base added for titration of H-montmorillonite (Wyoming bentonite).

If, now,  $pNa$  curves are drawn to the same scale as the pH curves we find a marked dependence of  $pNa$  upon concentration. The individual curves differ considerably from those which could be calculated on the assumption of complete ionization of Na (Fig. 50). Near the point of equivalence there is a very distinct reduction in slope, indicating a region in which base is being taken up with little ionization of the sodium.

This can be seen more clearly when cationic activities are plotted directly against base added (Figs. 54-57). The slope of the curve is then proportional to the fraction active. If the sodium salt were completely dissociated, the values for  $a_{Na}$  would fall on the broken curve, which, at low concentrations, may be taken as a straight line. Thus, by a comparison of the slopes of the two curves over any given range of additions of base one can see what the fate of the added cations has been. Fig. 54 presents the situation for the titration of Wyoming bentonite (montmorillonite) with sodium hydroxide. For very small additions of base, the curve is undefined, but its average

slope is considerably greater than that of the next part, from 15 to 70 milliequivalents base, which is practically linear. Then, from 70 to 85 milliequivalents, the activity remains practically constant; sodium is being added, but it is not ionized. On the pH curve this region immediately precedes the rapid change of slope which leads to the inflection point. From 85 to 100 milliequivalents, we find a very rapid rise in the activity curve.

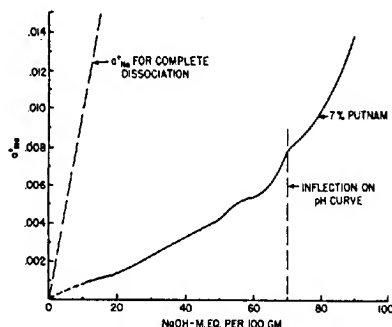


Fig. 55. Sodium ion activity plotted against base added for titration of H-beidellite (Putnam clay).

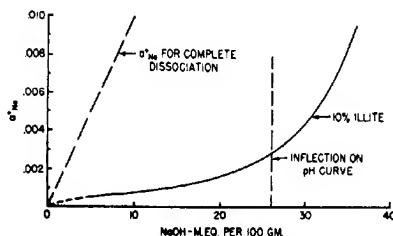


Fig. 56. Sodium ion activity plotted against base added for titration of H-illite.

The average slope is here about the same as that of the broken curve, indicating that the sodium added is completely ionized. This region lies on either side of the point of inflection on the pH curve. Finally, beyond 100 milliequivalents a reasonably constant slope somewhat less than that of the curve for 100% dissociation is attained. We have, therefore, no less than five distinct regions in the complete titration curve. The same situation is found, with somewhat less extreme changes of slope, in beidellite.

The curves for illite and kaolinite are smoother, with no rapid changes near the point of equivalence. They consist essentially of three regions: first, an undefined region with a relatively high fraction active; second, a region of fairly constant slope extending to about 70% of equivalence; finally,

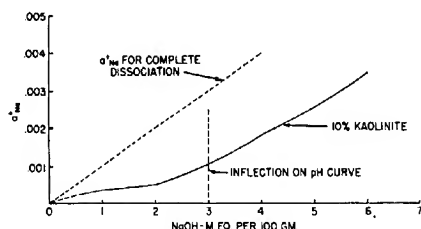


Fig. 57. Sodium ion activity plotted against base added for titration of H-kaolinite.

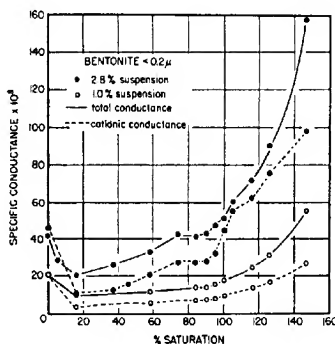


Fig. 58. Specific conductance, both total and calculated for cations only, plotted against percentage saturation with Na for two concentrations of Wyoming bentonite (montmorillonite).

a well marked rise to the point of equivalence and considerably beyond it. Kaolinite, however, differs from illite in the much higher value of the fraction active throughout the whole curve.

The comparison of the electrochemical properties of one clay mineral with another is made considerably more difficult by the complexity of the titration curves. If comparisons are made at the inflection point or at the

same fractional neutralization, it is still necessary to define the concentrations of clay which are to be used. This can best be done in terms of the total cationic concentration. In Table XIII comparable results for the five cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$  and  $\text{Ca}^{++}$  are given, but the total cation concentration changes from one clay to another. When the latter is held constant, such comparisons lead to the ionization order kaolinite > montmorillonite > beidellite > illite for the alkali cations, except in the ammonium clays where illite > beidellite. Hydrogen kaolinite appears as a weaker acid than the others, yet its salts are more strongly dissociated.

The order of the three alkali cations studied is not consistently the same for the four minerals, although ammonium generally gives a lower fraction active than sodium or potassium. With decreasing concentration of a given

TABLE XIII  
*The Ionization of the Clays*  
(Values at the point of equivalence of metallic cations)

Clay mineral	Clay concentration per cent	Exchange cation concentration moles/l.	Cationic fraction active*				
			$\text{Na}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{H}^+$	$\text{Ca}^{++}$
Kaolinite	10	.003	.34	.33	.25	.008	.080
Montmorillonite	1	.010	.21	.25	.18	.059	.022
Beidellite	1	.007	.09	.18	.08	.036	.015
Illite	5	.014	.10	.13	.12	.036	.040

\* This is the same thing as the activity coefficient in the case of a normal electrolyte; that is, it represents the ratio of the measured activity to the total cation concentration.

clay the fraction active falls. Earlier results on silver clays (12) suggest that a rise would eventually occur with increasing dilution.

The data thus far obtained on other clay minerals are fragmentary. From its potassium hydroxide titration curve, attapulgite appears to be the most highly dissociated clay yet found, both as the acid and the potassium clay. The electrochemical properties indicate that lattice substitutions are chiefly responsible for its being a true colloidal electrolyte (8, 17). The iron clay nontronite appears to resemble beidellite in its electrochemical properties (8).

A number of workers have presented pH titration curves for well-characterized clay minerals using divalent bases (Bradfield, 4; Bayer, 2; Mitra, 21; Mehlich, 20; Caldwell and Marshall, 8; Johnson and Norton, 11). In general, the changes in slope are more gradual than for monovalent bases, and the point of inflection lies at a lower pH value.

Extremely interesting relationships emerge when the membrane electrode technique is applied to the determination of divalent ions (16, 18). For all clays thus far examined the calcium activities are lower than the

sodium or potassium activities by a considerable factor; this is about  $1/2$  for kaolinite as against  $1/10$ – $1/20$  for clays of the montmorillonite group. Thus, divalent ions give very low cationic activity values, especially for the montmorillonite clays. The complete titration curves show the reason for this (Fig. 59). Over a considerable range of additions of calcium hydroxide the increase in calcium activity is extremely small. It is as though a practically nonionized compound were formed from about 30–70% neutralization. Then the activity rises sharply near the point of equivalence, although compared with that of monovalent cations it is still very low. Kaolinite shows this peculiarity less; its small exchange capacity makes all the calcium activities low, but they rise rapidly as base is added near the point of equivalence.

TABLE XIV

*Uptake of Sodium from NaOH by Clays on the Alkaline Side of the Apparent Point of Equivalence*

Clay	Concentration per cent	pH range	Fraction of added Na <sup>+</sup> active
Illite	5	8.62– 9.52	0.42
		9.52–10.26	0.70
Kaolinite	10	7.91– 9.75	0.73
		9.75–10.34	0.79
Montmorillonite	1	8.99– 9.69	0.55
		9.69–10.57	0.96
Beidellite	7	8.94–10.54	0.48

The distinction between cations held in the outer ionic atmosphere and those held internally is apparent in the case of the montmorillonite clays. With potassium, ammonium, and sodium it shows itself, as previously mentioned, in the narrow region where the cation is taken up with little ionization. Calcium displays a similar, but much broader, zone. A brief consideration of the sequence of changes which occur during these titrations gives a consistent explanation of these differences. In all cases we start out with a hydrogen-aluminum clay. The first additions of base react chiefly with the ionized hydrogen, replacing it by mono- or divalent cations as the case may be. In the case of the monovalent ions the ionic atmosphere is greatly expanded; the fraction active is relatively high. Further additions of base not only augment this process, but, in addition, contribute more and more ions to the interior, where their fraction active is low. Hence, on the average, we have, after the first small addition of base, a smaller fraction active, which remains relatively constant until the changes in the

ionic atmosphere are temporarily complete. Then, for a brief space, cations are taken up internally almost without ionization. However, just before the inflection on the pH curve, the outer atmosphere again becomes of predominant importance. Titration with a divalent cation, on the other hand, involves little change in fraction active as compared with hydrogen, and little change in the ionic atmosphere. Hence, after the first addition, the predominant effect is the uptake in the interior with its very low ionization.

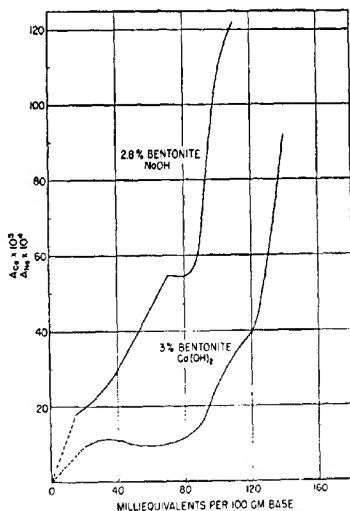


Fig. 59. Calcium ion and sodium ion activities plotted against base added in the titration of Wyoming bentonite. Note the difference in the vertical scales.

Near the point of equivalence, the outer ionic atmosphere begins to predominate through an increase in the charge. A second factor which may also be of importance is the distribution of  $c$  axis spacings. For calcium these tend to be more regular than for sodium or potassium. Any factor tending to impose such uniformity would also accentuate the differences between external and internal cations; the more so, the narrower the spacings.

The resemblance in the titration curves between kaolinite and illite is due to the fact that both ionize on external surfaces only. They differ in the fact that kaolinite probably holds cations chiefly by unsatisfied valencies

at the edges of the crystal, whereas illite, due to the substitution of  $Al^{+++}$  cation for Si in the silica sheets is able to hold cations rather tenaciously over the planar surfaces exposed. In beidellite and montmorillonite we have ionization also between the lattice units. All four clays show a relatively large fraction active for the first additions of base. This would be expected with any colloidal acid not completely dissociated, because cations in the outermost parts of the ionic atmosphere can be regarded as having higher activity coefficients than those closer to the surface. An interesting task for the future will lie in the exact interpretation of complete neutralization curves in terms of lattice replacements. A structural reason for the more strongly dissociating character of the montmorillonites as compared with the beidellites has already been mentioned (Chapter 6).

It should be emphasized that these structural interpretations are at present somewhat speculative. The undeniable fact revealed by the complete titration curves is that single cations are held with a wide range of bonding energies. From the relative changes in potential for given increments of base, it is possible to calculate the actual differences in energy of adsorption in calories.

The differences in the fraction active between the kaolinite and montmorillonite groups of clays on the one hand, and between the monovalent and divalent cations on the other, are destined to be of especial importance in soil science, plant nutrition, and plant ecology. The reason is that the uptake of cationic nutrients from the soil is a function of the activities of the ions with which the growing root is in contact; a function in which the balance or ratio between the different ionic activities is highly significant.

Further work is needed on the interpretation of titration curves on the alkaline side of the apparent point of equivalence. To a considerable extent both OH ions and alkali cations are taken up in nonionized form. Weakly acidic groups still function. Some representative data are given in Table XIV.

*Conductometric Titrations.* Although in dilute clay systems many points on the conductometric titration curves seem to fall on two straight lines which intersect at the point of equivalence (Bradfield, 3; Bayer, 2), the situation becomes much less simple at higher concentrations (Marshall and Krinbill, 15). It is then found that, once the pH has risen to a point where the conductance due to hydrogen can be neglected, the changes in total conductance parallel very closely the changes in cationic activity as measured by membrane electrodes. For instance, in the case of montmorillonite, the narrow region where sodium is taken up with little increase in activity shows correspondingly slight increase in conductance. Fig. 58 illustrates this case.

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## CHAPTER 11

### IONIC EXCHANGE REACTIONS OF THE CLAYS

#### *The Concept of Base Exchange Capacity*

The equivalence of cationic exchange reactions, known for many years to exist in natural soils and in the synthetic water softening agents, has led those concerned with the clay minerals to assume that each material can be characterized by its total exchange capacity. Bradfield's demonstration of the existence of an inflection point on the titration curve of an acid clay lent support to this assumption. As more data accumulated, however, it was seen that the position of the inflection point varied, both as regards pH and as regards quantity of base when different bases were employed. The variation in the pH at the inflection point is very striking when mono- and divalent bases are compared; the latter give the lower values. As regards the quantities of base necessary to reach the inflection point, a smaller variation is usually found. In the work of Bayer (beidellite, 3), Johnson and Norton (kaolinite, 25), and the author and associates (montmorillonite, beidellite, kaolinite and illite, 28, 29, 30) the monovalent cations gave closely agreeing values.

Mitra (32) draws attention to what he terms a specific cation effect upon the exchange capacity. The amounts of base needed to attain the respective inflection points fall in the order  $\text{Ca} > \text{Ba} > \text{Na}$ . On the other hand, the replacing power of these cations for hydrogen is in the order  $\text{Ba} > \text{Ca} > \text{Na}$ , which is the normal lyotropic series. He has shown also that titrations carried out in the presence of salts give higher values than those in which the base alone is used, in spite of the fact that the pH values at the inflection of the curves are significantly lowered.

Another method of investigation first used by Bradfield (7), and modified by Schofield (37), is to treat the clay with a mixture of base and salt, or salt and acid, until interchange is complete, using a whole series of mixtures of constant cation content and variable pH. The exchange capacity is then plotted against pH. This gives curves which for montmorillonite indicate good constancy of the base exchange capacity in acid solutions, but increasing values in the alkaline side. Here, three factors are probably important—the neutralization of the most weakly acidic groups, primary adsorption of OH ions, and decomposition of the clay to give soluble silicates at high alkalinities. In the interpretation of all these effects Mitra's comment that the exchange adsorption of the cations is more important than the combination of free  $\text{H}^+$  and  $\text{OH}^-$  ions to form water is exceedingly pertinent (32).

In view of these results it is not surprising to find that the leaching with different neutral salts has revealed a considerable variation in base exchange capacity. Salts of divalent bases tend to give higher values than those of monovalent bases. One reason for this (see below) is the possibility of the formation of "basic" salts with the clay and a soluble anion, for instance Clay - (ZnOH)<sup>+</sup>.

#### *Cationic Exchange in the Clays*

Although soil scientists have long been aware of the importance of cation exchange (42, 43), it is only in recent years that exact quantitative studies of well-defined clay minerals have been undertaken. Following earlier work on the permutites, Jenny and coworkers have determined the exchange isotherms for a number of cations on beidellite (Putnam clay, 18, 15). The order of ease of entry by exchange was  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{H} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{La} < \text{Th}$ . However, in the divalent series the order depended to some extent upon the cation originally present, whereas the monovalent series was entirely consistent. In the release of polyvalent cations, irregularities were sometimes found. The release of Mg and Ca by barium gave curves which cross, so that at low concentrations of Ba, Mg appeared to be held more tightly than Ca. The two factors of greatest importance are valency and hydration. It is possible, however, that comparative hydration figures for aqueous salt solutions are somewhat misleading, since the hydration of the cation which is anchored to the clay may be affected by the silicate structure itself.

Nevertheless, Wiegner's rules (44) still afford the best generalizations yet propounded covering the colloid-chemical behavior of clay suspensions. For ions of equal valency, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace when already present upon the clay. Furthermore, clays saturated with highly hydrated cations are themselves more highly hydrated and are more difficult to coagulate than clays saturated with slightly hydrated cations. In agreement with this, the *zeta* potentials of clay particles in suspension follow the order  $\text{Li} > \text{Na} > \text{K} > \text{Rb}$  and  $\text{Mg} > \text{Ca} > \text{Ba}$ . In all such series hydrogen is exceptional. For the most part, it behaves like a slightly hydrated di- or trivalent ion. Exceptions to these rules arise where the crystalline silicate structure itself makes specific demands upon the cations. Thus, certain clays subjected to drying are able to fix cations of appropriate sizes in a non-exchangeable form. The primary condition is the size of the dehydrated ion, not its valency nor its size when hydrated.

Certain criticisms of the hydration theory have been put forward. The ionic hydration numbers usually quoted are expressed in molecules of water per ion. The magnitude and, in certain cases, even the relative order

of these numbers, varies with the basis chosen for comparison. Furthermore, the hydrogen ion always appears exceptional. Bär and Tendeloo (2) have suggested that the polarizability constant of the cations provides a more reliable guide than their hydration numbers. As regards exchange constants, Jenny (19) related the values of  $K$  in the Wiegner equation  $y = K \left( \frac{c}{a - c} \right)^{\frac{1}{2}}$  to the ionic radii which are determined for the anhydrous ions by X-ray data. However, until a truly quantitative theory becomes available, the Wiegner concept has the great advantage of affording a simple mental picture.

Other complications also arise. Certain polyvalent cations, zinc for example, may undergo exchange in two ways—as  $\text{Zn}^{++}$  and also as  $\text{ZnCl}^+$  or  $\text{ZnOH}^+$  (22). This accounts for the abnormally high exchange capacities found when zinc is used as the exchange cation. In acid solution, part of the zinc is nonexchangeable. This is supposed to be attached by one valency firmly to the silicate surface while the other permits anion exchange of chloride, nitrate or hydroxyl. Bower and Truog (6), using montmorillonite with a considerable variety of bases, found that the increase in exchange capacity with weak polyvalent bases such as beryllium, copper, ferric iron, and thorium, was very great (100–200%) when determinations were made in aqueous solution, but that use of methyl alcohol as solvent gave practically normal values. The effect is, therefore, ascribed to hydrolysis; ions such as  $(\text{BeOH})^+$ ,  $\text{Cu}(\text{OH})^+$ ,  $\text{Fe}(\text{OH})_2^+$ , or  $\text{FeOH}^{++}$ , being attached to the clay surface. Montmorillonite, beidellite, illite, and Cecil clay (probably kaolinite) all showed the increases.

Adsorption isotherms for various cations, using montmorillonites, kaolinite, and ground micas, have been obtained by Schachtschabel (36). His results differ significantly from those of Jenny (19), and Jenny and Gieseking (15), who used Putnam clay (beidellite). For entry into ammonium montmorillonite, the order found was  $\text{Li} < \text{Na} < \text{H} < \text{K} < \text{Rb} < \text{Cs}$ . Hydrogen falls in the middle of the monovalent series, whereas, in Jenny's experiments with beidellite, it was clearly the most effective in displacement. The same order was found for kaolinite, hydrogen being less effective than rubidium or caesium in displacing  $\text{NH}_4^+$ . On comparing the two clay minerals, ammonium was found to be more firmly held by kaolinite than by montmorillonite. The quantitative results with ground micas may not be exactly comparable with those of natural clays of the illite group, but Hendricks and Alexander (17) have shown that, in the latter, hydrogen enters much more vigorously into the exchange complex than for montmorillonite or kaolinite.

The whole situation is thus essentially confused as far as comparisons of one mineral with another are concerned. Partly, this is due to the different

experimental techniques employed. Thus, Jenny used Putnam clay prepared by electrodialysis and subsequently treated with the appropriate base. No drying of the clay occurred at any stage. Schachtschabel prepared his ammonium clays by salt leaching and subsequent washing, finally drying to a fixed humidity in a desiccator. Since, however, such drying causes fixation effects with ammonium clays of the montmorillonite and illite groups, the subsequent exchange equilibria will differ greatly from those obtained by Jenny's method. Hence, it is not a valid criticism of the hydration theory to quote Schachtschabel's ionic series against it, as has been done by Grim (16).

The extent of replacement of calcium by hydrogen and by barium has been studied by Allaway (1) using two bentonites, illite and kaolinite. In the entry of hydrogen the order was kaolinite  $>$  illite  $\geq$  bentonite, in agreement with the uptake of calcium by plants from these colloids. Only minor differences were found with barium.

Not only is there considerable variation in strength of binding of a given cation by different clay minerals, but, in certain cases, a given mineral shows different affinities for a given cation, depending upon the previous history of the clay. This was demonstrated by Wiegner and Mitchell (43) for permutites, and extended to the clays by Wiegner and Renold (43). Mixed ammonium-calcium clays were prepared, in the one case by action of calcium chloride upon ammonium clay, and in the other by treating calcium clay with ammonium chloride. These reactions were carried out with such quantities that the same proportions of Ca and  $\text{NH}_4$  were present in the two cases. The two mixed systems were then allowed to react separately with calcium chloride and ammonium chloride solutions. It was found both for  $\text{NH}_4$  and Ca that the ion which had been present initially upon the clay was more firmly bound than if it were introduced later. The difference was greatest for a permutite, large for a kaolinite clay, but relatively small for bentonite (montmorillonite). More recently Bottini (5) has followed the thermal curves for loss of ammonia from the mixed Ca- $\text{NH}_4$  and  $\text{NH}_4$ -Ca systems. In these experiments permutite and bentonite showed significant differences in  $\text{NH}_4$  binding according to previous history, while kaolinite clay did not. In studying the exchange of  $\text{NH}_4$  and Ca upon bentonites, Vanselow (40) had previously found different equilibrium constants depending on which ion was originally present upon the clay. Barium-calcium and barium-copper interchanges did not show the hysteresis.

#### *Theory of Cation Exchange*

Three approaches to the quantitative expression of base exchange have been made. In the first, thermodynamic arguments involving more or less crude approximations have led to various mass action equations (Kerr, 26;

Rothmund and Kornfeld, 35; Vanselow, 40). Davis (12) has recently criticized these formulations from the theoretical viewpoint. In the second, empirical equations derived from, or connected with, adsorption isotherms were used (Wiegner, 42; Jenny, 18; Vageler, 39).

An examination of the equations based on both approaches was made by Marshall and Gupta (27), who showed that none was entirely satisfactory over a wide range for beidellite or montmorillonite clays.

### *Jenny's Theory*

The third approach is based on an improved kinetic treatment of surface ionization in which each ion can be regarded as having a certain mean oscillation volume (Jenny, 19). Exchange becomes possible when oscillation volumes overlap, but its actual occurrence depends on the entering ion getting between the original ion and the surface. Equations have been derived only for interchange between ions of the same valency. This theory has led to a better understanding of the behavior of heteroionic systems and has brought into the foreground of discussion two hitherto neglected effects: surface diffusion and contact exchange.

a. *Simple Exchange* (19). For a reaction in which an electrolyte like KCl is added to pure Na clay the equation derived takes the form

$$W^2 \left( 1 - \frac{V_K}{V_{Na}} \right) - W(S + N) + SN = 0.$$

Where  $N$  represents the amount of KCl initially added,  $W$  is the amount of exchange, *i.e.*, of potassium entering or sodium expelled,  $S$  is the saturation or exchange capacity and  $V_K$  and  $V_{Na}$  are the oscillation volumes of potassium and sodium ions respectively. As may readily be seen by inspection, this equation predicts (1) that when  $N$  is very large,  $W$  approaches  $S$ , that is, exchange approaches completion for high concentrations of electrolyte; (2) when the oscillation volume of the ion added exceeds that of the ion on the clay, then the exchange is less than in the contrary case. In other words, a large oscillation volume corresponds to a large hydration, which means a low replacing energy.

b. *The Complementary Ion Principle* (20). From slightly more complex equations, which deal with exchange from clays containing mixtures of cations, conclusions of great importance to soil science emerge. Thus, where two cations are present initially upon the clay the replacement of the one is greatly affected by the oscillation volume of the other, or complementary, ion. Compare, for example, a 50:50 sodium-potassium clay with a 50:50 hydrogen-potassium clay in exchange experiments with ammonium chloride. Consider first an infinitesimally small exchange. The ratio sodium/potassium released will be the same as the ratio sodium ion activity/po-

tassium ion activity in the clay system, since the measurement of ionic activities is based on the work done in an infinitesimally small transfer from the system under consideration to a standard solution. Similarly, the ratio hydrogen/potassium released will be identical with hydrogen ion activity/potassium ion activity. From what has been said previously about the dissociation of the clays it is evident that the former ratio will not differ very greatly from 1.0, while the latter will have a value of 0.10 or less. Considering now the exchange situation, very much more potassium will be released from the hydrogen-potassium clay than from the sodium-potassium clay for the same small exchange. This situation will also present

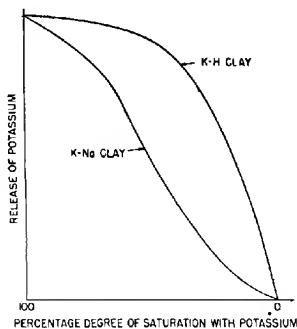


Fig. 60. Diagram according to Jenny and Ayers showing the release of potassium from potassium-hydrogen and potassium-sodium systems.

itself for the finite exchanges which occur as increasing concentrations of ammonium chloride are used. Theoretically, with sufficient ammonium chloride to cause complete exchange, the final ratios potassium/sodium and potassium/hydrogen will each be unity. Now let us concentrate attention upon the release of potassium alone. Instead of considering one initial composition, take the whole range from 0–100% saturation with potassium in each case and plot the fraction or percentage of potassium released for a given treatment with ammonium chloride against the degree of saturation with potassium (Fig. 60). Two distinct curves are obtained for the K-Na and K-H systems. Except at the two ends where the curves necessarily meet, a higher proportion of the total potassium is released by exchange from the K-H clay than from the K-Na clay. In general, we may state that the release of a given ion is proportionately greater, the smaller the oscillation volume of the complementary ion.

*c. Surface Diffusion.* The overlapping of oscillation volumes upon a given surface would rapidly lead to a random distribution where mixtures of ions are concerned. No direct evidence on this point is available for clays. In cation exchange experiments with zeolites and salts with small cations and large anions it provides the chief mechanism for exchange. From what we know of the montmorillonite clays it is easy, however, to calculate the mean planar surface per exchange spot and to compare the situation with the ionic distribution in salt solutions. A montmorillonite with an exchange capacity of 100 meq./100 g. has about 0.7 exchange spots per unit cell of 24 oxygens. The total planar surface of the latter is twice the unit cell dimensions or about  $90 \text{ \AA}^2$ . The mean distance apart of the exchange spots is thus about  $11 \text{ \AA}$ . This may be compared with the mean  $\text{K}^+$  ion -  $\text{K}^+$  ion distance in potassium chloride solutions;  $N = 11.8 \text{ \AA}$ ,  $N/10 = 14.9 \text{ \AA}$ . Even allowing for the fact that only a fraction of the exchange spots afford complete dissociation of the exchange cation, it is clear that, statistically speaking, overlapping of oscillation volumes is a strong probability. It must be remembered also that for a considerable distance, measured outwards from the surface, the exchange cations are, on the average, nearer together than in their distribution along the surface.

*d. Contact Exchange (21).* The overlapping of oscillation volumes by adjacent colloidal particles can lead to exchange of ions between them, a process known as contact exchange. It can operate between dissimilar particles provided they have the same sign of charge. Experimentally, it is difficult to separate this process from that of ionic migration due to surface diffusion. Jenny has shown that the combination of the two processes leads to a very rapid movement of ferrous ions in bentonite gels. The application of these ideas to problems encountered in the transfer of cations from the soil to the plant root forms an important topic in plant nutrition studies. It has already been shown that in some cases this process predominates over uptake from a simple salt solution.

#### *Hidden Assumptions and Uncertainties*

In practically all the theoretical deductions made on base exchange reactions the implicit assumption has been that ions of a single kind all belong to one set, that is, all are held by bonding energies of the same magnitude. This is equivalent to regarding the acid clays as possessing a single dissociation constant, which, as we have already seen, is a considerable oversimplification. The other cations probably also show a wide distribution of bonding energies. This is clearly evident when cation activity measurements are made at different degrees of saturation. Table XV indicates that, even when the extreme acid and extreme alkaline conditions are left out of consideration, marked variations in the fraction active are found. In the



case of montmorillonite the sudden drop in fraction active over a rather narrow zone from 70 to 85% neutralization with sodium hydroxide is followed by an almost explosive increase. With calcium hydroxide we have a broad zone practically of zero activity followed by a marked rise. These differences probably go back to structural features peculiar to the expanding lattice clays. Kaolinite shows a steady rise in the cationic fraction active for sodium, but with calcium there is also a region of slight increase in calcium ion activity with increasing amounts of base.

This great variation in fraction active, and in energy of adsorption shown by a given cation upon a given clay, emphasizes the artificial nature of Jenny's assumption of a single oscillation volume. It is not surprising then

TABLE XV  
*Variation in the Fraction Active of Na<sup>+</sup> and Ca<sup>++</sup> With Successive Stages of Neutralization*

Clay	Concentration per cent	Na <sup>+</sup>		Ca <sup>++</sup>	
		Neutral- ization per cent	Fraction active	Neutral- ization per cent	Fraction active
Montmorillonite	2.8-3.0	35- 55	0.28	30- 50	<0.001
		55- 70	.30	50- 70	.002
		70- 85	.04	70- 90	.008
		85-100	1.19	90-110	.031
Kaolinite	10	17- 33	.13	40- 59	.049
		33- 67	.20	59- 80	.156
		67-100	.63	80- 99	.195

that base exchange experiments afford oscillation volume ratios for pairs of cations which are very different from the corresponding activity ratios. For one thing, base exchange experiments involve the removal of relatively large amounts of cations, whereas activity measurements correspond theoretically to the withdrawal of infinitesimally small quantities. Second, the ionic environment of the dissociating clay is considerably different in an exchange experiment, with its large addition of soluble salt, from the much more "dilute" environment provided by the dissociating clay alone. This is particularly true for the hydrogen ion and for divalent cations.

#### *The Exchange of Ions of Differing Valencies.*

The mathematical formulation of exchange reactions between ions of differing valencies has on all sides encountered serious difficulties. Wiegner's modification (18) of the Freundlich adsorption equation was based on the observation that cation exchange reactions differed from the ordinary adsorption of molecules at interfaces in one important respect. The exchange equilibrium, using fixed total amounts of reactants, was stated to be inde-

pendent of the volume of the system. Later work has shown that this is true only for interchanges between ions of the same valency. A distinct dependence upon volume is found where the ions differ in valency. Davis (12) recently examined both the strictly thermodynamic and the statistical kinetic theory of ion exchange. Neither afforded a satisfactory formulation for ions of differing valencies.

The reason for the existence of a volume effect in the exchange of ions of differing valency lies in the fact that, energetically considered, more is accomplished than where the participating ions have the same valency. Osmotic work must be done in changing the numbers of active ions, in addition to what would normally be considered the heat of reaction. This osmotic work term will naturally vary with the total concentration employed. To some extent this same effect is present, even with ions of the same valency, whenever the fraction active differs for the two ions. Wiegner's rule thus merely expresses the fact that similar ions, such as sodium and potassium, are ionized from the clays to approximately the same extent. The studies of the author and his coworkers substantiate the conclusion that K,  $\text{NH}_4$ , and Na clays are not widely different in their ionization. However, silver clays and hydrogen clays dissociate much less and exchanges between, say  $\text{Na}^+$  and  $\text{Ag}^+$ , would accordingly be influenced by the total volume of the system.

#### *Cationic Fixation Effects*

Soil chemists have devoted considerable attention to processes by which exchange cations may be rendered non-exchangeable and therefore less readily available as nutrients for plants. In several of these contributions, well-defined clay minerals have been employed. Attention was first directed to potassium, which, under alternate wetting and drying, changed in part to a nonexchangeable form (41). This property was shown to be characteristic of clays of the montmorillonite (23, 24) and illite groups (8), and is absent from those of the kaolin group. It is especially strongly shown by beidellite and illite clays; hence its great importance in midwestern soils of the United States, where these clays predominate. A reduction in total exchange capacity accompanies the change. Theoretically, we would expect this to be exactly equivalent to the potassium fixed if the change consists in the movement of potassium to mica-like positions in the crystal lattice. In many cases this is true, but some exceptions, not fully explained, have been recorded (24).

Other cations also participate in these reactions (9), the dominant factor being ionic size. Ions which are of such size that they fit into the places occupied by potassium in potash micas, show the strongest tendency to become nonexchangeable. These geometrical factors have been particularly

well emphasized by Page and Baver (34), who investigated the displacement of exchange equilibrium due to drying for a number of cations on bentonite (Table XVI). Barium, similar in ionic radius to potassium, became less readily removed by exchange after the barium clay had been dried. Sodium, lithium, and calcium clays, on the other hand, were relatively less affected. The presence of large organic cations, such as diethyl ammonium, prevented the reduction in exchangeability caused by drying, presumably by holding the silicate layers permanently apart.

There is good reason to believe that a sluggish reversible equilibrium exists between the exchangeable ions and those which have previously been

TABLE XVI  
*Displacement of Equilibrium Caused by Drying (Page and Baver)*

(The Miami soil colloid, a beidellite clay, was employed. The figures give the percentage replacement by hydrogen ions when the latter was equal in amount to the saturating ion. Drying was at 100°C.)

Cation	Ionic Radius Å	Exchange		Difference
		Moist per cent	Dry per cent	
Li <sup>+</sup>	0.68	89.7	74.6	15.1
Na <sup>+</sup>	0.98	89.4	72.4	17.0
NH <sub>4</sub> <sup>+</sup>	1.21	71.65	34.6	37.05
K <sup>+</sup>	1.33	76.95	35.1	41.85
Rb <sup>+</sup>	1.48	54.4	26.65	27.75
Cs <sup>+</sup>	1.67	43.8	24.05	18.75
Mg <sup>++</sup>	0.71	65.0	46.1	18.9
Ca <sup>++</sup>	0.98	82.0	68.7	13.3
Sr <sup>++</sup>	1.15	59.5	43.2	16.3
Ba <sup>++</sup>	1.31	72.35	38.25	34.1

fixed by drying. The latter are slowly liberated again under appropriate conditions (8).

It can readily be seen that these fixation tendencies may greatly modify the usual relationship between ionic hydration and valency of the exchange cation and the colloid-chemical properties of the clay. The previous history of the clay now becomes of great importance. Mattson first noticed that the swelling of K-saturated montmorillonitic clays was greatly reduced by previous drying (31), and many other properties are similarly affected.

#### *The Adsorption and Liberation of Anions*

In colloid chemistry generally, it is often held that hydroxyl ions are very effectively adsorbed by negatively charged surfaces, leading to an increase in the charge and in the *zeta* potential. In any given case, however, it is difficult to decide whether the process is really a simple adsorption or whether there occurs a reaction between an already existing acidic group

upon the surface and the hydroxyl ion. This dilemma faces us squarely in the case of the clay minerals. It is well known that all the clays can take up bases, with consequent reduction in the pH of the alkali, well on the alkaline side of the apparent point of equivalence. Study of the complete titration curves, as previously mentioned in Chapter 9, shows that the major part, both of the hydroxyl ions and of the associated cations, is fixed in nonionized form over a broad range of alkalinities beyond the point of equivalence.

Evidence that weakly acidic groups are largely responsible for this behavior is afforded by the results of titrations carried out using mixtures of hydroxides and chlorides. The presence of a neutral salt greatly increases the amount of base needed to attain a given pH. This would not be expected if there were simply an adsorption of OH ions above the point of equivalence. It is difficult to see how the chloride ion could increase such an adsorption. On the other hand, if difficultly replaceable hydrogen is present, either a salt solution or an excess of base would bring it into reaction. As mentioned previously, the situation is further complicated by the partial decomposition of the more reactive clays at high alkalinities, by which alkali silicates are formed.

The Indian workers (32) see in the "specific ion effect," by which, on the alkaline side of the neutral point, the order becomes  $\text{Ca} > \text{Ba}$  instead of  $\text{Ba} > \text{Ca}$ , evidence that OH ions are adsorbed. Surface hydroxides are then produced, their effectiveness being greater as their solubility is lower.

Whereas, in the adsorption of cations, processes of ionic replacement operate almost exclusively, the uptake of anions by the clays involves in some cases replacement, and in others addition. In either case, however, the site of the reaction is believed to be exposed hydroxyl. It may be present as a surface of the planar lattice or it may be accidental, in the sense that it occurs at crystal edges where unsatisfied valencies have operated.

Very clear evidence of the ready replacement of hydroxyl by fluorine has been given by Dickman and Bray (14). The liberation of hydroxyl caused a well marked increase in the alkalinity of the suspension. It will be recalled that  $\text{OH}^-$  and  $\text{F}^-$  are practically of the same size. Hence, their exchange involves no lattice rearrangements and the only factor preventing complete substitution of F for OH lies in the lack of accessibility of most OH groups. In clays of the kaolinite group only OH groups on outer planar surfaces and on edges are accessible. However, in the hydrated halloysite known as endellite all OH groups should eventually be accessible, since kaolinite units are separated by double layers of water molecules into which  $\text{F}^-$  ions might readily penetrate. In the montmorillonite clays accessible OH groups are only on the crystal edges. Those present within the gibbsite layers are probably inaccessible.

In the case of phosphate also, there is evidence of an interchange of  $\text{OH}^-$  and  $\text{H}_2\text{PO}_4^-$  ions, but now the character of the surface is entirely changed and the final effect is really an addition. The  $\text{PO}_4$  group projects, as it were, from the original surface, sharing the position of one original OH group within that surface. Since this tetrahedral grouping of oxygen around phosphorus is similar to that around silicon, we can regard this adsorption as an extension of the original lattice. Murphy (33) first showed that finely ground kaolinite takes up phosphate very extensively at low pH values, the quantities involved being several times the cation exchange capacity. Stout (38) then examined the reaction both chemically and by X-ray studies. He showed that OH groups, made accessible by grinding, reacted with phosphate ions with loss of water. The final result was that the characteristic X-ray lines of kaolinite still present in the original ground samples had disappeared from the phosphated product, which was amorphous. However, on removal of the phosphate, the kaolinite lines reappeared. Stout states that all accessible  $-\text{OH}$  groups react with the phosphate, the effect of previous grinding being to render a high proportion of the OH groups accessible. From what has been said in Chapter 9 regarding the effect of fine grinding it is by no means certain that kaolinite was under investigation, but rather a mixture of the unchanged mineral with a considerable proportion of amorphous permutite-like material.

This aspect of Murphy's and of Stout's experiments has been clearly emphasized by the work of Coleman (10) and of Black (4). Both workers examined unground kaolinite freed from iron and aluminum hydroxides by preliminary treatments. The amounts adsorbed from very dilute phosphate solutions were small and not highly dependent upon the pH, although Black found evidence of a maximum at pH 5-6. Other clay minerals, montmorillonite, illite and halloysite, gave similar results. However, with kaolinite, high concentrations of phosphate, on long standing, gave much higher adsorption at pH 3 than at pH 7. It would thus seem that the major effect investigated by Stout was less a property of kaolinite than of the permutite-like material produced by fine grinding.

The exchange experiments of Dean and Rubins (13), in which phosphate adsorbed on kaolinite clays is removed by treatment with arsenate, afford evidence that the relatively rapid adsorption from dilute solution is a property of the exposed  $\text{Al}-\text{OH}$  groups at the crystal edges. It was found that the anion adsorption capacity was approximately equal to the cation exchange capacity for kaolinitic clays. This would naturally be the case where edge  $\text{Si}-\text{OH}$  groups are responsible for the base exchange, and similarly situated  $\text{Al}-\text{OH}$  groups for the anion exchange. In the montmorillonite and illite groups the anion adsorption would only amount to a small fraction of the cation exchange capacity since the latter is associated chiefly with ionization over the planar surfaces.

It has generally been assumed that ions such as chloride and nitrate are not appreciably adsorbed by pure clay minerals. Mattson (31), indeed, interpreted experiments on the Donnan equilibrium, in such a way as to show an apparent negative adsorption of chloride, sulphate, and ferrocyanide, the effect increasing in the order given.

A somewhat different light has been thrown on the situation by the work of Schofield (37). In strongly acid solution, clays can take up both potassium and chloride ions, the former greatly predominating. The chloride is exchangeable for other anions, just as the potassium is for other cations. The uptake of anions rapidly diminishes with decreasing acidity and, for neutral or slightly acid systems, is negligibly small. His interpretation is in good agreement with what we now know of the structure of the clay minerals. It may be amplified somewhat as follows.

In the montmorillonite-beidellite and hydrous mica clays we have permanent negative charges upon the planar silicate surfaces. At the edges, however,  $\text{Si} - \text{OH}$  and  $\text{Al} - \text{O}^-\text{H}$  groups are present. The former are weakly acidic and contribute to the increase in exchange capacity in alkaline media. The latter provide the site for anion adsorption. In the kaolinite clays there is little or no permanent charge. Accidental anion and cation adsorption is of predominant importance. Since the ratio of  $\text{Al} - \text{O} - \text{H}$  to  $\text{Si} - \text{OH}$  at the edges is now 1:1, whereas in the montmorillonite group it is 1:2, the anion adsorption comes even more prominently into the picture. Dean and Rubin's observation that phosphate and arsenate adsorption are approximately equivalent to the cation exchange capacity for kaolinite clays fits very neatly into this picture.

#### *The Donnan Equilibrium*

Far-reaching conclusions regarding swelling, hydration, the electrical double layer, and ionic exchange reactions of the clays, have been based by Mattson (31) on the theory of the Donnan equilibrium. Apart from the specific papers devoted to this subject, his writings since 1929 have been so permeated with these deductions that it is extremely difficult to trace what has and what has not been confirmed by experiment, and furthermore which experiments have been performed upon valid Donnan systems and which have not. To clarify the matter a brief general discussion of Donnan systems is required.

We are here concerned with the ionic equilibria between ordinary electrolytes and colloidal electrolytes when the latter are under a constraint tending to prevent their attaining complete chemical equilibrium. Thus, in the case illustrated in Fig. 61 (a), which was the type first considered by Donnan, the membrane constrains the large colloidal anions, and, since electrical neutrality must be preserved, the associated cations are equally prevented from entering the outside solution. However, molecular species



Having appreciated these considerations and utilized corresponding data, Mattson then attempted to extend the argument to the case of individual colloidal micelles or charged surfaces, as illustrated in Fig. 61 (c). From the negatively charged surface an atmosphere of sodium ions extends outward, their volume concentration diminishing with increasing distance. Beyond a certain plane the solution becomes essentially of constant composition. This latter now corresponds to the outer solution of the first two examples, and the imaginary plane takes the place of the membrane. The inside solution, however, no longer has constant composition, and a whole series of Donnan equilibria, varying with distance from the surface, would be needed to describe it. The system is obviously not amenable to experimental treatment, since there is no means of sampling the inner or outer solutions. Their plane of separation is indeterminate and could, of course, vary enormously in position in different experiments. It seems, therefore, that this case is theoretically much more complex than Mattson realized. Since, in addition, it is experimentally indeterminate, calculations based on the simple Donnan equations derived for the first two cases above, pass here into the realm of pure speculation. Thus, as Davis (11) has pointed out, the potential difference calculated by Mattson from the different chloride concentrations on the two sides of his experimental membranes, is nothing more nor less than the membrane potential itself, and has no precise significance in relation to the electrical double layer or ionic atmosphere of each individual clay micelle.

Turning now to some of Mattson's experimental results obtained with systems of type A, we find the remarkable conclusion that the degree of dissociation of sodium bentonite increases with increasing concentration of sodium salt in contact with it. No satisfactory explanation has been offered. It is at variance with more recent work on mixtures of potassium clays and potassium salts by Marshall and Bergman (28), in which the actual potassium ion activities were measured. The only certain conclusion one can at present draw is that better experiments are needed.

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## CHAPTER 12

### ELECTROKINETIC PROPERTIES OF THE CLAYS

#### *Surface Potentials*

Before taking up in detail the important researches which have linked the electrokinetic properties of the clays with other aspects of their behavior, it is important to discuss some very general relationships in colloid chemistry. Consider a single negatively charged planar surface AB (Fig. 62) whose charge is balanced by cations in the liquid. Following Gouy and later investigators, the distribution of these cations follows an exponential law in relation to the distance from AB. For this reason, pursuing the analogy of the earth and the air above it, the ions are spoken of as forming an atmosphere about the surface. It is statistically maintained by the balance between the electrical attraction of unlike charges and the Brownian movement of the ions. One can think of the latter as a pressure exerted outwards. Unlike a gaseous pressure, however, it is caused by the presence of a second type of molecule—the solvent dipole. These orient themselves around and between the charged units and in so doing give rise to a second kind of variation with distance from the surface. Close to the surface the solvent dipoles are in a very intense electric field between positive and negative charges; they are therefore largely oriented. As the distance from the surface increases the field rapidly diminishes and with it the degree of orientation of the solvent dipoles. At certain relatively short distances from the surface the molecular properties become indistinguishable from those of the solvent in bulk. Thus, the ionic and molecular properties vary simultaneously with distance from the surface. Both are affected when other molecules, ions, or charged surfaces are introduced into the system. Modern theory has attempted to find quantitative laws governing these variations.

Three groups of phenomena are involved, corresponding to which three potentials or potential functions have been employed. In the past, this led to some confusion. With the help of diagrams such as that of Fig. 63, first introduced by Freundlich (5), two of these are easily distinguished. The quantitative theory of their relationship to one another is still incomplete. In Fig. 63, let the total electrical work in moving unit charge from the surface of the solid to a remote point in the liquid be  $-\epsilon_0$ , represented by the height  $Oy$  along the ordinate. Distances outward from the surface are measured along the abscissa  $Ox$ . The quantity  $-\epsilon_0$  is the Nernst potential of the surface on an arbitrary scale in which the remote parts of the liquid phase are assumed to be at zero potential. This single potential  $-\epsilon_0$  can-

not be measured, but where it is combined with another similar potential an electrochemical cell results. By keeping one potential constant, variations in the other can readily be measured. The only effective ions are those in chemical equilibrium with the interface; all others act only in-

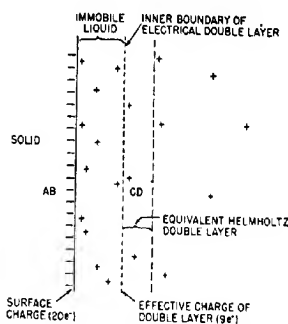


Fig. 62. Relationship of surface ionization to the electrical double layer.

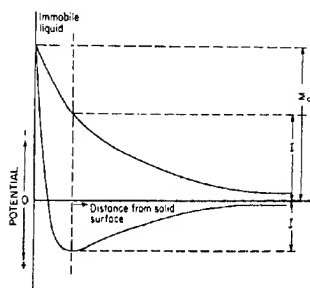


Fig. 63. Freundlich diagram illustrating the electrokinetic or zeta potential ( $\zeta$ ) and the thermodynamic or Nernst potential ( $\epsilon$ ) and their independence of one another.

directly by influencing their activities. The relationship between potential and variation in mean activity of effective ions is that given by the Nernst equation:  $E_1 - E_2 = \frac{RT}{nF} \ln \frac{a_1}{a_2}$ ; where  $E_1$  and  $E_2$  are the potentials measured at the respective activities  $a_1$  and  $a_2$  of effective ions whose valency is  $n$ .

Consider now what happens when an electric field is applied parallel to the surface AB. The liquid is, in general, set in motion; the effect is known

as electroendosmosis. After much discussion, first among distinguished physicists and later among colloid chemists, the following properties were ascribed to this system. It was agreed that the movement of the liquid is quite different from that in ordinary pressure flow. The bulk of it moves with constant velocity, corresponding, therefore, to plug flow in a tube. Near the wall, however, two other layers of liquid may be distinguished. That nearest the surface is immobile. One can regard it as strongly adsorbed. Then follows a thin layer in which the velocity varies from zero up to its maximum value. The electrical properties may be described in many alternative ways. Helmholtz treated the layer of liquid having variable velocity as if it were bounded by two plates of an electrical condenser. The electrokinetic, or *zeta*, potential was related to the charge and to the distance between the plates by the usual condenser formula. Gouy later showed that this very rigid picture, difficult to reconcile with the properties of ions, could be replaced by one more flexible, in which the ions formed an atmosphere extending outward from the surface. The distance  $d$  between the plates of the imaginary Helmholtz condenser was shown to be a sensitive function of the ionic concentrations in the outer liquid. The *zeta* potential can, therefore, be defined as the work done in moving unit charge from the plane CD to a remote point in the liquid.

Freundlich first pointed out that the charge per unit area in the plane CD might differ both in magnitude and in sign from that ascribed to the surface of the solid AB. Changes in the outer solution may cause quite different variations in the *zeta* and the Nernst potentials, depending upon their effect within the immobile layer of liquid. In Fig. 63, two extreme cases are shown, in which the same Nernst potential  $E_0$  is associated in the one case with a *zeta* potential of the same sign, and in the other with one of the opposite sign. In some classical experiments on glass surfaces, Freundlich and Rona showed that the Nernst potential responded to changes in the outer liquid only through effects upon the hydrogen ions with which the glass maintained an equilibrium. The *zeta* potential on the other hand showed the usual lyotrope series for ions of the same valency. The effect of cationic valency was very strong, divalent ions reducing the charge to zero at low concentrations while tri- and tetravalent ions caused a reversal, the *zeta* potential becoming positive. Under suitable conditions, the Nernst potential could be maintained constant while these drastic changes in the *zeta* potential were effected.

The third potential, or potential function associated with ionized surfaces, has to do with the ions themselves rather than the surfaces. A definite amount of electrical or osmotic work is required to transfer ions at each specific distance from the surface, to a standard solution. There is, of course, no means of isolating such layers of ions for experiment. If, however, one

such distance  $d_i$  is chosen, it is easy to measure the potential corresponding to the electrical work done in moving an average ion which resides between  $d_i$  and the surface from this environment to a standard solution. Defining  $d_i$  for a surface in contact with a liquid is equivalent to defining the concentration of a colloidal system. Hence, if we set up an electrochemical cell of the type

Calomel-Sat. KCl/Clay-H<sup>+</sup>//Glass membrane//

//Standard H<sup>+</sup>Cl<sup>-</sup>/Sat. KCl Calomel

in which the glass membrane acts as a medium for the transfer of hydrogen ions only, the potential measured can be used to define the mean activity of all the hydrogen ions associated with the clay. This is what is done in a pH measurement on a clay-water system. The formula used is again the Nernst equation  $E = \frac{RT}{nF} \ln \frac{a_1}{a_2}$  but this potential  $E$  should be very sharply distinguished from  $E_0$  as described above.

Of the three, the *zeta* potential is the most closely connected with the general stability of colloidal systems. A very complete account of it is given in Abramson's monograph (1). Work on the clays and on the permittivities has proved of decisive importance in tracing these relationships. Before discussing results a brief but critical outline of methods will be given.

#### *Cataphoresis Measurements on the Clays*

The small particle size of natural clays largely precludes determinations of the *zeta* potential by measurements based on electric endosmosis. The converse effect, known as cataphoresis, movement of particles relative to the liquid under the influence of an electric field, has found ready application.

The Helmholtz-Smoluchowski equation for cataphoretic movement is deceptively simple:

$$\zeta = \frac{4\pi\eta v}{HD}$$

The *zeta* potential  $\zeta$  is directly proportional to the linear velocity  $v$  of the particles moving under an applied field  $H$  in a liquid of dielectric constant  $D$  and viscosity  $\eta$ . Size and shape do not enter into the formula. The measurement of  $v$ , however, is complicated by the fact that the colloidal system must be viewed while in motion. Movement in bulk involves the use of boundary fluids, as in the Burton U tube method. In such a moving boundary it is very difficult to keep the electrical conditions constant during measurement. Alternatively, the movement of individual particles may be followed in the ultramicroscope. Here, in addition to difficulties caused by

the random Brownian movement, there is an endosmosis of the liquid in the cell. The latter, however, can be allowed for in cells of well defined shape. Theoretical uncertainties regarding  $D$  and  $\eta$  also arise, since it is by no means certain that the liquid within the electrical double layer will be identical with that in bulk. The situation was further complicated when Debye and Hückel announced that the correct factor in the formula was 6, not 4. A few years later, a reexamination of the theory by Henry showed that the original formula was correct for electrical insulators of any shape, but that conducting particles gave different factors for different particle shapes. The present situation with regard to the clays is exceedingly confused. Some measurements have been made using the factor 4, others using the factor 6. It is reasonably certain that clays of the kaolinite and illite groups can be treated as electrical insulators. The montmorillonite clays conduct internally, they are certainly not insulators, but this fact has never been taken into consideration in evaluating the results of cataphoresis experiments.

#### *The Zeta Potential and Coagulation*

As Hardy, Powis and Burton showed, the *zeta* potential is the most important factor governing the stability of dilute lyophobic sols. Below a certain critical potential, coagulation sets in. There are actually two critical potentials. The first corresponds to the point at which union of particles on collision first becomes possible; that is, it represents the critical potential for the start of slow coagulation. The second critical potential corresponds to the beginning of rapid coagulation, when all collisions between particles lead to union. This can perhaps best be appreciated by placing two curves upon the same diagram, Fig. 64. The solid curve represents the number of particles  $n_t$  remaining in a sol  $t$  seconds after addition of electrolyte, plotted against the concentration of the latter. The other curve represents the *zeta* potential plotted against concentration. The data presented, taken from Tuorila's monumental paper (16), are for kaolinitic clay. The zones of stability, slow coagulation, and rapid coagulation are clearly evident. Using this same clay, Tuorila also showed that, on the acid side of the neutral point, very similar curves were obtained for coagulation by a variety of mono- and divalent cations. The *zeta* potential was plotted against the time needed to attain a certain stage of coagulation (Fig. 65). Considering the fact that the divalent cations coagulate at much lower concentrations than the monovalent, the close agreement in the curves shows that, in absence of disturbing factors, a general theory of coagulation could be based on the *zeta* potential. This has been attempted by Müller (14).

Disturbing factors, however, are especially marked in the case of the clays. One, first noted by Odén (15), concerns the sensitivity to coagulation

of particles of different sizes. Odén found that in a polydisperse clay suspension of somewhat indefinite mineralogical nature, the coarser particles were coagulated at lower concentrations of electrolyte than the finer.

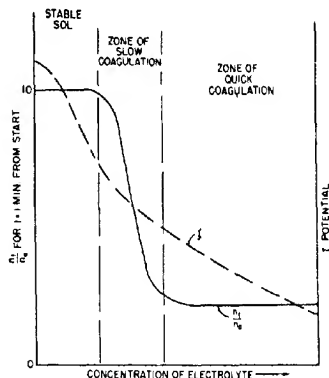


Fig. 64. Relationship between coagulation, (fraction of original particles present after a fixed time), and concentration of electrolyte, and between zeta potential and concentration of electrolyte.

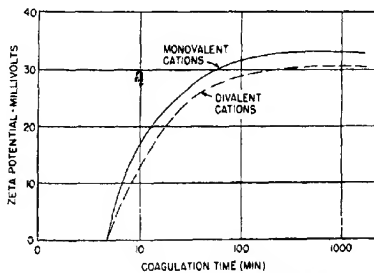


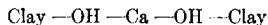
Fig. 65. Relationship between zeta potential and the logarithm of the time taken to attain a given stage of coagulation. (Tuorila.)

Tuorila explained the decreasing fraction of effective collisions as slow coagulation progressed by reference to Odén's experiment. In a study of monodisperse fractions of a bentonite, Hauser and Le Beau (8) observed that the cataphoretic velocity of 20  $m\mu$  particles was about 14% greater than that of 96  $m\mu$  particles. On the other hand, the theoretical considera-



tions discussed by Abramson (1) lead to the conclusion that small spherical particles would have a lower cataphoretic velocity than particles whose radius is large compared with the thickness of the electrical double layer, assuming both to have the same surface charge density. In the coagulation of dilute bentonite sols with potassium hydroxide, Hauser and Reed (9) found that from ten to twenty times as much electrolyte was needed for the 14 m $\mu$  fraction as for the 87 m $\mu$  fraction. All fractions gave the same titration curve, indicating that they were essentially pure montmorillonite.

A second disturbing factor arises in the coagulation of clays in alkaline solutions. It was noted by Gedroiz (7) and Comber (3) for clays derived from soils, and by Mattson (11) for bentonite, that these sols were more sensitive to coagulation by divalent cations in alkaline solution than in neutral or slightly acid solution. Mattson (11) showed that an increased adsorption of the divalent cation was found alongside the usual strong uptake of hydroxyl ions. He therefore suggested that the increased sensitivity is due to the formation of particle-particle linkages through polyvalent cations. Schematically, one could have



This explanation was challenged by Tuorila (16), who found a similar effect with a kaolinite clay. He demonstrated, as had Mattson, that the coagulation can occur at abnormally high values of the *zeta* potential, although this was not invariably the case. In these alkaline solutions no consistent relationship between *zeta* potential and rate of coagulation was found. Since the effects were particularly marked with bases which form sparingly soluble hydroxides, Tuorila was inclined to regard the increased sensitivity as due to the accumulation of insoluble hydroxide on the surface. The system, then, is no longer a pure clay suspension, but a mixture of negatively charged clay with positively charged hydroxide, the latter partially coating the clay particles.

#### *The Charge Density and the Thickness of the Electrical Double Layer*

Gouy, in his investigations of the properties of the diffuse double layer, showed that the model of an electrical condenser introduced by Helmholtz could still be retained. He found that the effective distance apart of the plates of the imaginary condenser was a sensitive function of the external ion concentration. The theory has been amplified by Müller and Abramson (see 1), and it is now possible to calculate the effective thickness of the double layer and the surface density of charge for large particles, knowing the *zeta* potential and the ionic concentration in the intermicellar liquid. For flat surfaces the condenser formula used is

$$\zeta = \frac{4\pi d\sigma}{D}$$

where  $d$  is the effective thickness of the double layer,  $\sigma$  the surface density of charge, and  $D$  the dielectric constant. Thus variations in  $\zeta$  can be due to variations either in  $d$  or  $\sigma$ . It is only possible to separate these factors by the use of other equations connecting two of the three quantities. Müller and Abramson derive a relationship between  $\sigma$  and  $\zeta$  which, in the general

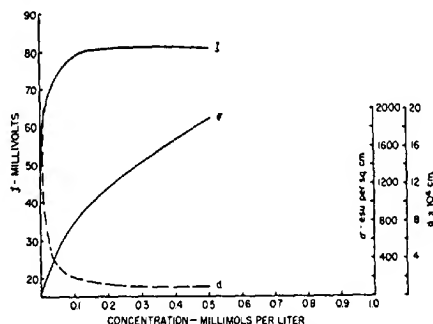


Fig. 66. Variation in zeta potential ( $\zeta$ ) charge density ( $\sigma$ ) and effective thickness of the double layer ( $d$ ) on addition of sodium hydroxide to hydrogen kaolinite. (Coughanour and Utter.)

case of an intermicellar liquid containing any number of positive ions of type  $i$  and negative ions of type  $j$  is as follows:

$$\sigma = \sqrt{\frac{NDkT}{2\pi \times 1000}} \sqrt{\sum c_i (e^{-z_i(e\zeta/kT)} - 1) + \sum c_j (e^{+z_j(e\zeta/kT)} - 1)}$$

For the simpler case of a uni-univalent electrolyte for which  $c_i = c_j$  and  $Z_i = Z_j = 1$  this reduces to

$$\sigma = 2 \sqrt{\frac{NDkT}{2\pi \times 1000}} \sqrt{c} \sinh \frac{e\zeta}{kT}$$

which, on evaluation of the constants, becomes

$$\sigma = 2\alpha \sqrt{c} \sinh \frac{\zeta}{\beta}$$

where  $\alpha = 17,650$  and  $\beta = 0.025$  volt at  $18^\circ\text{C}$ . These formulae are well adapted to the case of the clays because they are derived for flat surfaces. For further details the reader should consult Abramson's monograph.

Coughanour and Utter (4), in their investigation of the electrokinetic properties of three kaolinite fractions (0.2 – 0.4  $\mu$ ), (0.4 – 0.8  $\mu$ ) and (0.8 – 1.6  $\mu$ ), have utilized these equations to calculate  $\sigma$  for various additions of sodium hydroxide to hydrogen kaolinite. Fig. 66 shows how the

three quantities  $\zeta$ ,  $\sigma$ , and  $d$  vary with the amount of base. In these experiments all the additions were more than sufficient to change the hydrogen clay to a sodium clay. The two larger fractions gave entirely similar results to the  $0.2 - 0.4 \mu$  fraction.

The author in addition has utilized these equations to calculate  $\sigma$  and  $d$  for two interesting cases investigated by Tuorila (16), also for a kaolinite clay. Fig. 67 shows the effects of sodium chloride additions, Fig. 68 those of calcium chloride. With increasing concentration of electrolyte,  $\zeta$  and  $d$  both fall but  $\sigma$  rises and approaches constancy. The form of the  $\sigma$ -concentration curve, is similar to that of an adsorption isotherm of the Langmuir

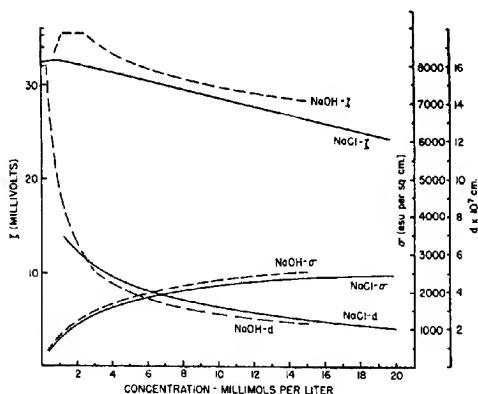


Fig. 67. Comparison of the effects of NaOH and NaCl upon the zeta potential ( $\zeta$ ), charge density ( $\sigma$ ), and effective thickness of the double layer ( $d$ ) for kaolinite. (Calculated by the author from Tuorila's data.)

type. For sodium chloride solutions Tuorila's recalculated data indicate that the limiting charge density on kaolinite surfaces approaches 2500 electrostatic units per square centimeter. This would correspond to about one electron/2000  $\text{\AA}^2$ . This, it must be remembered, is not the charge at the solid surface, but the equivalent charge on the immobile layer of liquid in contact with the solid surface.

#### *The Zeta Potential in Relation to the Exchange Cation*

Baver (2) measured the zeta potential during the course of neutralization of Putnam clay (beidellite) with different monovalent and divalent bases. His work is especially important because measurements of pH, specific conductivity, migration velocity, and viscosity were made upon the same

systems. In agreement with Mattson (13), who had previously used bentonite clay with sodium and calcium hydroxides, Bayer showed that close

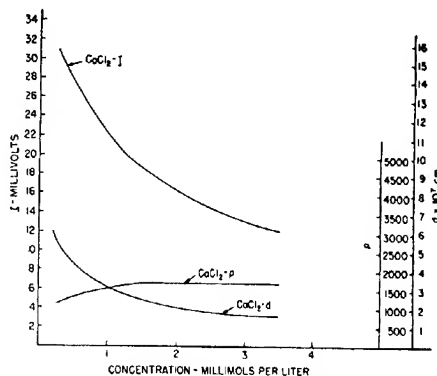


Fig. 68. Variation in *zeta* potential ( $\zeta$ ), charge density ( $\rho$ ), and effective thickness of the double layer ( $d$ ) for additions of calcium chloride to kaolinite (calculated by the author from Tuorila's data).

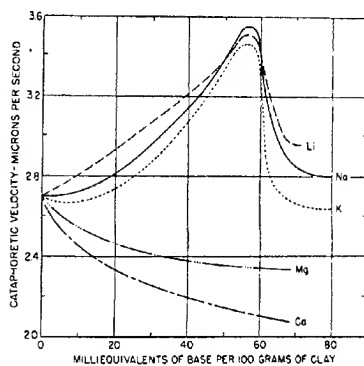


Fig. 69. Variation in cataphoretic velocity upon addition of mono- and divalent bases to hydrogen beidellite (Putnam clay. Bayer's data.)

to the point of equivalence the *zeta* potential attained a sharp maximum for monovalent bases, whereas divalent bases gave a continuous decrease. The curves are presented in Fig. 69. The order is  $\text{Li} > \text{Na} > \text{K}$  in the case

of the monovalent cations (except for a single point) and for the divalent cations,  $Mg > Ca$ . Jenny and Reitemier (10) obtained similar results, which they related to the diameters of the dehydrated ions.

At this point it is of interest to compare the cataphoretic velocities observed by different investigators upon relatively pure clay systems (Table XVII). The actual velocities in  $\mu/sec./volt/cm.$  are given rather than the calculated *zeta* potentials. Compared with the others, the values obtained by Hauser and Reed for monodisperse bentonites, and by Coughanour and Utter for monodisperse kaolins, are high.

TABLE XVII  
*Cataphoretic Velocities of Clay Particles in Dilute Suspension*  
( $v$  is in  $\mu/sec./volt/cm.$ )

Reference	Clay type	Concentration per cent	Cataphoretic velocity when saturated with				
			H	Na	K	Mg	Ca
2	Putnam (Beidellite)		2.7	3.6	3.5	2.3	2.1
8	Bentonite (20 $m\mu$ )	0.24		7.0			
13	Bentonite	0.1	2.75	4.3	3.8		
13	Sharkey (Montmorillonite-Beidellite)	0.04	3.2	3.7			1.9
4	Kaolinite (0.2-0.4 $\mu$ )	0.001	4.2	7.0			

#### *Effect of Anions*

Mattson (13) is one of the few investigators who have concerned themselves with the effect of the ion having the same sign of charge as the colloidal particle. The following results were obtained with a dilute sodium bentonite sol. In a comparison of sodium chloride, sulfate, and ferrocyanide, at concentrations up to 0.04  $N$ , he found an increase in *zeta* potential with increasing amounts of salt, the order being  $Cl < SO_4 < Fe(CN)_6$ . This was also the order of the amounts of the respective salts needed for coagulation. Thus, polyvalent anions function as stabilizers. Mattson related this to swelling phenomena and to the effect of the anions upon the Donnan equilibrium between the interior of the particles and the external environment (12).

It should be pointed out in connection with Mattson's work, that his assumption that the clays have an amphoteric character is not borne out by cataphoresis experiments on pure kaolinite and montmorillonite clays, which remain negative and show no reversal of charge in acid solution. As previously noted, the chemical behavior of their broken edges does display limited amphoteric properties.

#### *The Influence of Cations on Coagulation*

Although the coagulation of clays by various salts had been observed and commented upon earlier, the detailed study of ionic series began with

the work of Gedroiz (7). This Russian investigator was interested in the factors which determine the dispersibility of different soils in water. Clearly visualizing the importance of the clay fraction and of its capacity for base exchange, he prepared a series of clays and soils with different exchange cations. Their ease of peptization in water and their coagulation with different salts were then followed. In this way it was shown that the ease of peptization followed the series  $\text{Li} > \text{Na} > \text{K}$ . The sensitivity toward coagulation by added electrolytes followed the converse order  $\text{K} > \text{Na} > \text{Li}$ , and this same order held for the coagulating action of added salts.

The most exact and thorough experiments yet made on coagulation by electrolytes were carried out in Wiegner's laboratory at Zürich. Three

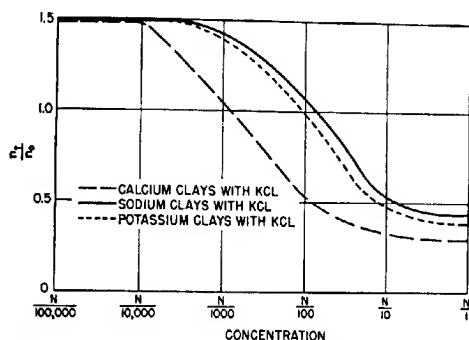


Fig. 70. Effect of the exchange cation upon the clay on coagulation by a single salt. (Gallay's data.)

methods were used: ultramicroscopic counts, observations of turbidity and settling, and measurements of viscosity. Special attention was paid to the effects of cation exchange and to the separation of the two factors ionic hydration and valency (17). The experiments of Gallay (6) were carried out on the clay fraction separated from a loess soil. Its mineralogical nature was not established. Tuorila's results (16) were obtained on a kaolinitic clay, and extensive comparisons were made between the behavior of dilute suspensions of this clay with similar systems comprised of permutites and of quartz. In these investigations the relationship to the zeta potential was, as we have seen, strongly emphasized.

Fig. 70, taken from Gallay's results, shows how the sensitivity toward coagulation by a single salt varies with the nature of the cation already present upon the clay. The zones of slow and of rapid coagulation are shifted toward the lower concentrations for the calcium and potassium clays as compared with sodium clay. The difference between potassium

and sodium is relatively small; that between calcium and potassium is very large.

Fig. 71 compares coagulations by potassium and calcium chlorides. Tuorila has given extensive data in which kaolinitic clay was coagulated by a variety of chlorides. The time for visible flocculation was plotted logarithmically against the logarithm of the concentration. The monovalent cations form a group in which the effectiveness increases from Li to Cs, and for the divalent ions similarly from Mg to Ba. The hydrogen ion is even more effective than the divalent ions.

In reviewing the electrokinetic properties of the clays, it is evident that clear relationships to chemical structure and to the detailed mechanisms by which clays ionize have not yet been established. This is not surprising

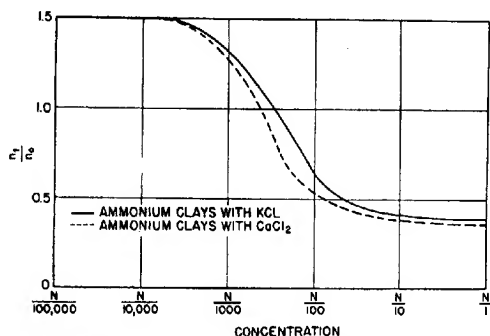


Fig. 71. Comparative effect of potassium and calcium in the coagulation of an ammonium clay. (Gallay's data.)

when we recall that the *zeta* potential comprises only a part of the total ionic atmosphere. That portion immediately adjacent to the silicate wall which is comprised within the immobile layer of liquid is not considered in electrokinetic theory. This part, richest in ions and situated in the most intense part of the electric field created by the charged silicate surface, shows itself clearly in other electrochemical properties; in potentiometric and conductometric titrations, for example, and in ionic exchange reactions. The electrokinetic properties, on the other hand, reflect the electrochemistry of the silicate surfaces only at second remove. Thus, it is not surprising that the detail of this relationship has thus far not been clearly traced.

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## CHAPTER 13

### THE MECHANICAL PROPERTIES OF CLAY SUSPENSIONS, SOLS AND PASTES

Because of the technical importance of plasticity, an enormous literature has grown up around the mechanical properties of clay-water systems. Here we shall only attempt to select those items which reveal most clearly the general colloid-chemical principles. Three properties have been investigated; viscosity in dilute sols, thixotropy in sols and gels of intermediate concentration and plasticity in the pastes. Of the three, only viscosity is well defined physically. Three different conceptions of thixotropy are current and the definition of plasticity has been the subject of much discussion and controversy.

#### *Viscosity and Thixotropy*

The chief interest in measurements of the viscosity of dilute clay suspensions has lain in departures from the ideal conditions as predicted by Einstein for small spherical particles. Several causes have been discussed. The primary particles are markedly nonspherical. They possess an electrical double layer; long range forces acting between particles must therefore be taken into consideration. Hydration may vary. Finally, coagulation may cause the formation of loosely aggregated structures. The addition of electrolytes to a clay suspension affects simultaneously two, three, or four of these factors. It is, therefore, not surprising that the interpretation of viscosity measurements should have been distinguished more for its diversity than for its clarity. To add to the confusion, relatively few measurements have been made on well-defined clay minerals of known particle size.

In the montmorillonite group the viscosity relationships are more interesting and complex than for kaolinite. The influences of particle size and of concentration have been accurately established by Hauser and Le Beau (11), using carefully fractionated and electrodialedyzed Wyoming bentonite. As would be expected for any hydrophile colloid, the viscosity increased markedly with decreasing particle size. The simple Einstein equation was only obeyed for low concentrations of the coarsest particles studied.

The addition of bases to electrodialedyzed clays causes extremely interesting changes in viscosity, first pointed out by Mattson in the case of montmorillonite (bentonite) (14), and Bayer (3) in the case of beidellite (Putnam clay). It was found that, with increasing amounts of monovalent base,

there was an increase in viscosity which attained a maximum just before complete neutralization. Then a marked decrease occurred, followed by a second rise and a maximum at concentrations of added base or salt sufficient to cause coagulation. Bayer showed, with divalent ions, that after an initial decrease only the increase consequent upon coagulation is found (Fig. 72). The first maximum is less marked with potassium than with

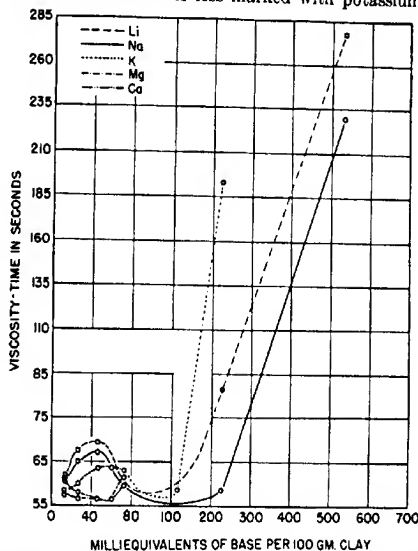


Fig. 72. Variations in the viscosity of Putnam clay suspensions upon addition of bases. (Bayer's data.)

lithium or sodium, suggesting that the hydration associated with the exchangeable ion is the major factor. The curves show a different order for the second rise in viscosity, namely,  $K > Li > Na$ . The great coagulating power of the K ion now causes extensive aggregate formation and, hence, high viscosity at concentrations where the sodium and lithium systems are still relatively well dispersed.

More recently Mukherjee, Gupta and Indra (16) have followed viscosimetrically the changes occurring when sodium hydroxide is added to hydrogen bentonite. Yield values and consistency pass through maxima just before the point of equivalence, then fall, and finally rise again with a large excess of base.

As the concentration of montmorillonite clay is increased, each of these viscosity maxima eventually becomes a zone of thixotropy (7). It is thus possible to prepare two thixotropic systems at the same concentration of clay. In the one, characterized by a high *zeta* potential and high hydration, long range interparticle forces must be evoked to explain the mechanical properties of the gel. In the other, characterized by a low *zeta* potential, a considerable excess of base or salt, and by the formation of aggregates, the normal processes incident upon coagulation are assumed to operate. Hence, this second zone of thixotropy can be observed at much lower concentrations of clay than the first. The existence of these separate zones of thixotropy has caused considerable confusion in the literature; some authors (7, 13) have concerned themselves with the first, others (11) with the second.

The behavior of kaolinite, carefully fractionated according to particle size, has been discussed by Norton, Johnson and Lawrence (17). They have utilized a conception of thixotropy, first introduced by Goodeve and Whitfield (8), differing materially from Freundlich's original definition which employs a different method of measurement. Freundlich regarded thixotropy as an isothermal gel-sol transformation which could be measured in a relative way by determining the setting time, subsequent to liquefaction by agitation. The authors cited above now define thixotropy in terms of the departure of the sol system from the ideal behavior of a Newtonian liquid under shearing stress. The actual setting to a gel no longer features in this approach. The thixotropy is defined as the limiting slope of the viscosity-reciprocal shear curve when the latter tends to zero, that is, for infinitely high rates of shear. The actual determination is therefore carried out in the Couette or similar type of instrument using variable shear rates.

The discussion of thixotropy by Green and Weltman, in an extremely thought-provoking article (9), makes it seem doubtful that the quantity measured by the Goodeve and Whitfield method is really a thixotropic coefficient. It would be out of place to discuss their concept in detail, as their experiments were not concerned with clays but with suspensions of pigments. Nevertheless, future experiments using clays will have to be designed with Green and Weltman's work in mind. Briefly, they regard thixotropy as the property responsible for hysteresis effects in viscosity-rate of shear curves. However, such measurements cannot, in their opinion, be used to evaluate single thixotropic constants. They believe that future progress will lie in a somewhat different approach—the treatment of thixotropic structure formation and breakdown as rate processes akin to chemical reactions.

Norton, Johnson and Lawrence (17) found empirical equations connecting viscosity, thixotropic coefficient, and yield point, each with concentra-

tion. The effect of particle size varied according to the cationic state of the kaolinite. The hydrogen clay (a flocculated system) showed a marked increase in viscosity with diminishing particle size; the deflocculated sodium clay only showed clear regularities when the viscosity was plotted against the mean interparticle distances for the various fractions. At equal viscosities the relative spacings between particles were about the same, as may be seen from their figure.

The neutralization of hydrogen kaolinite with sodium hydroxide (16) showed, in contrast to montmorillonite and beidellite, a very marked decrease in viscosity near the point of equivalence. Further additions caused no change; the data did not extend far enough to show coagulation by a large excess of base.

#### *General Theory*

The nature of the internal forces which cause clay suspensions to assume their peculiar viscosimetric and thixotropic properties has been keenly debated. Hamaker, Verwey, and others have examined the general theory of particle and double layer interaction and have come to the conclusion that repulsive forces predominate in very dilute stable colloidal systems. To explain the thixotropic properties of more concentrated, uncoagulated systems van der Waals' attractive forces are assumed to come into play. Langmuir (12) has strongly criticized this approach and, in an explanation of the formation of oriented tactoids in concentrated colloidal systems, he balances attractive forces between colloidal micelles and ions of opposite sign of charge against osmotic repulsive forces originating in the ionic atmospheres. His conclusions, in turn, have been adversely criticized by Verwey (19).

It would seem that the clays would provide very appropriate material for the testing of these theories since the mathematical difficulties for the case of the interactions of flat parallel plates are much less than for those of small spherical particles. Langmuir and Verwey agree that the repulsive force between parallel plates is given by the equation

$$K = 2nkT (\cosh u - 1)$$

where  $K$  is the force,  $n$  is the ionic concentration,  $kT$  is the usual gas constant per ion, and  $u$  is defined by  $u = ve\psi/kT$ ,  $v$  being valency of the ions which balance the surface charge,  $e$  the electronic charge and  $\psi$  is the potential at a point midway between the plates. The difficulty with this equation, according to Verwey, is that  $\psi$  cannot be determined without further simplifying assumptions and, in order to avoid these, he considers the energy of interaction rather than the force. At equilibrium this energy of repulsion is balanced against the energy of attraction caused by van der

Waals-London forces which extend outward from the surface and fall off inversely as the square of the distance between the plates. The total energy as a function of plate distance is then found to follow curves of two possible types (A and B, Fig. 73). In A, corresponding to stable sols, the maximum prevents union of the particles on collision, whereas in the case of B there

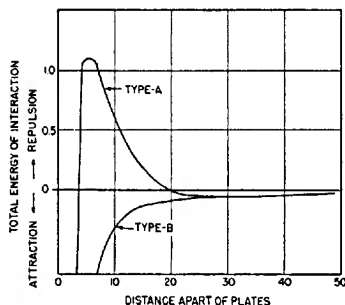


Fig. 73. Verwey's diagram relating the total energy of interaction of platy particles to the distance apart of the plates.

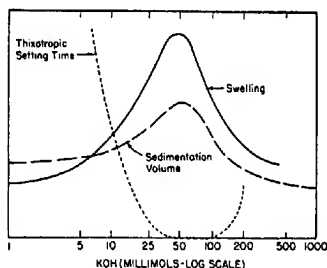


Fig. 74. Variations in swelling, sedimentation volume and thixotropic setting time for additions of potassium hydroxide to hydrogen bentonite. (Freundlich, Schmidt and Lindau.)

is a net attraction at all distances and coagulation proceeds unhindered. In curves of type A, in addition to the maximum there is also a weak minimum at larger distances, which finally diminishes to zero as  $d$  increases still further. This minimum would probably be sufficient to account for the thixotropy of uncoagulated systems at fairly high concentrations and high *zeta* potentials.

Up to the present, data suitable for a rigorous testing of these equations are not available. Experiments on the swelling pressures of the clays do not involve complete parallel orientation of plates. Verwey's curves show that, from the maxima outward in the case of type A, and throughout in the case of type B, a roughly exponential relation exists between the total energy of interaction and the distance apart  $d$  of the plates. Now  $d$  is roughly proportional to the water content, while the energy of interaction

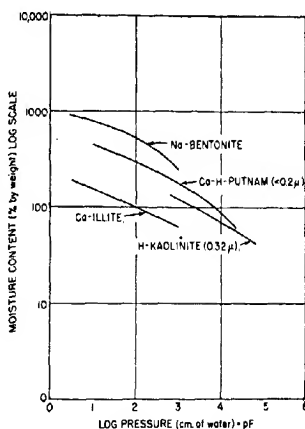


Fig. 75. Relationship between pF and logarithm of the moisture content for bentonite (Mattson), kaolinite (Johnson and Norton), Putnam clay and illite (Woodruff).

is proportional to the capillary potential of the system. Hence, if the logarithm of the moisture content is plotted against the logarithm of the capillary potential or the swelling pressure a roughly straight line relationship should be found. This is actually the case, as may be seen from Fig. 75. Thus, there is semi-quantitative agreement, at least, between the available data on clay systems and the Verwey theory.

#### *Plastic Properties*

Although various definitions of plasticity have been propounded, no generally accepted basis for quantitative measurement has been arrived at. The idea of permanent deformation under stress is present in most of these definitions, which are usually elaborated to include other aspects of plastic properties, such, for instance, as the fact that a certain yield value must be exceeded before plastic deformation begins, and that the normal

elastic relationships of solids under stress play only a minor role. Thus, instead of measurements of plasticity, we have many quantitative investigations dealing with plastic flow, and side by side with them, entirely different measures of the moisture range over which plastic properties are found. This diversity in experimental approach is in part due to the fact that certain plastic properties are shown by solid-liquid mixtures not usually thought of as having characteristic plasticity. Thus, relatively coarse sand can be mixed with water to give a mouldable material, but the mixture differs from the plastic clays in the fact that it does not retain its shape upon drying. The various combinations of solid and liquid properties characteristic of the plastic region are now grouped together under the term

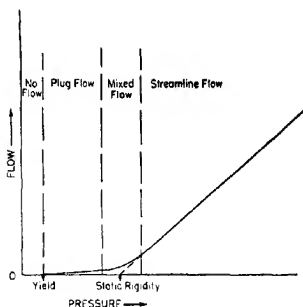


Fig. 76. Flow of clay pastes in capillary tubes. (Scott Blair.)

Rheology. For a detailed classification of these properties the reader is referred to works of Scott Blair (6) and of the Dutch group of investigators (1).

*Plastic Flow.* The characteristic features of plastic flow are readily understood by a comparison with ordinary viscous flow as in Fig. 76. Four stages are distinguished as increasing pressure is applied. *A.* No flow occurs until a certain critical stress at the wall of the tube is reached. This experimental yield value is required to overcome the adhesion of the outer layer of clay to the tube. It is possible that due to the adsorption of water by the tube surface, the outermost layer can be regarded as a water envelope. *B.* With increasing pressure beyond this yield value, the clay moves as a solid plug and can be envisaged as sliding through the outer envelope of water. In this region the volume flow is proportional to the pressure. *C.* With further increases in pressure the critical shearing stress of the clay system itself is reached, first for the outermost layer and then for succeeding layers of

smaller radius. The flow is, therefore, mixed in character. Beyond the layer showing critical stress we have streamline flow, within it, plug flow. This region gives an upward bending curve. *D*. Finally, the plug disappears and we have streamline flow, analogous to that of a pure liquid but differing from the latter in that it is represented by a straight line showing a definite intercept upon the pressure axis. This intercept has been given the name "static rigidity" by Scott Blair and "shearing strength" by Buckingham. The slope of the line is proportional to the pseudo-viscosity (Scott Blair) of the system. For thixotropic substances it is also a measure of the thixotropic coefficient, according to Goodeve and Whitfield. This illustrates how these concepts may overlap, and in fact, uncovers a serious weakness in the Goodeve and Whitfield theory, since practically all solid-liquid systems would yield such a thixotropic coefficient, irrespective of any tendency to set to a solid.

The question then arises, which of the constants of a flow experiment, yield value, static rigidity or pseudo-viscosity comes nearest to a quantitative measure of plasticity? The answer seems to be that it is unreasonable to expect a single constant to express all that is meant by plasticity. Furthermore, there is no comprehensive theoretical basis for combining the separate constants into a single measure. Thus, it is not surprising that there should be a wide divergence of opinion among rheologists on this matter. This shows itself very clearly in the numerous designs of "plastometers" now in use. The modern trend seems to be toward instruments capable of yielding complete shearing stress-rate of shear curves.

The connections between the flow constants and such variables as the mineralogical nature of the clay, the nature of the exchange cation, particle size, *etc.*, are only partially worked out. Fig. 77 presents a part of Scott Blair's results for a bentonite, the Rothamsted clay fraction (largely beidelitic), and a kaolin clay. The curves connecting static rigidity with volume concentration are all similar in general shape and show that, for the swelling clays, a high static rigidity can be attained at a much lower clay concentration than is the case with the kaolinitic clays.

The relation between yield point and clay concentration (by volume) has been examined for various hydrogen kaolinite fractions by Norton, Johnson and Lawrence (17). The results agree with an equation of the type

$$\text{Yield point} = k C^n$$

where  $n$  was 3 for all the fractions (from  $10\mu$  to  $0.28\mu$ ) examined, whereas  $k$  increased rapidly with decreasing particle size. The corresponding sodium clays all gave vanishingly small yield points, which suggests that a very important factor in determining the magnitude of the yield point is the extent of aggregation of the original clay. The sodium clays were more



completely dispersed into their ultimate particles than were the hydrogen clays. This is in line also with the fact that the viscosity of sodium kaolinite is less than that of hydrogen kaolinites.

*The Atterberg Constants.* Instead of considering plasticity in relation to forces, Atterberg, in a comprehensive study of the plastic properties of soils (2) introduced the idea of constants defining the moisture range over which plastic properties are observable. These are (A) the upper plastic limit which represents the transition from the fluid to the stiff consistency;

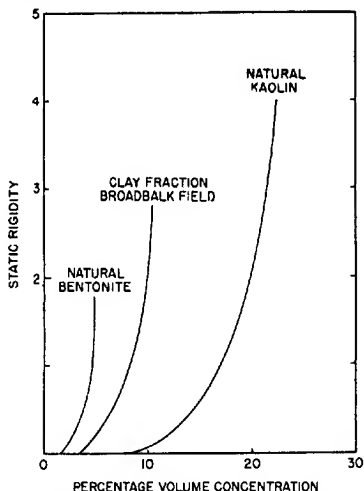


Fig. 77. Relationship between static rigidity and clay concentration. (Keen and Scott Blair.)

(B) the lower plastic limit which is the lowest moisture content at which the material still remains plastic; and (C) the plasticity number or plastic index which is the difference between (A) and (B). Bayer (5) has given an illuminating discussion of the significance of these constants.

"The lower plastic limit represents the moisture content of the change from the friable to the plastic consistency. Orientation of particles and their subsequent sliding over each other take place at this point, since sufficient water has been added to provide a film around each particle. Experimental evidence shows that cohesion is a maximum at the lower plastic limit. The moisture content of this limit depends upon the amount

and nature of the colloidal material present. The colloid content regulates the number of films and the nature of the colloid determines the quantity of water that is adsorbed before a distinct water film around each point of contact is formed. This is substantiated by the fact that a high degree of correlation exists between the hygroscopicity over 30%  $H_2SO_4$  and the moisture content of the lower plastic limit."

"The upper plastic limit signifies that moisture content at which the water films become so thick that cohesion is decreased and the soil mass flows under an applied force. It also depends upon the number of films that are present; essentially, it is the moisture content at which most of the films coalesce to fill up the majority of the soil pore space."

These considerations enable us to predict in a qualitative way the major variations in the Atterberg constants. Thus, in comparing swelling and nonswelling clays of the same particle size, it is evident that the former will have the higher plastic limits since they take up water internally as well as externally. The plasticity numbers, however, will be closely similar, since they are dependent chiefly on the number of external water films. For a given clay, reduction in particle size will increase the plasticity number. The fact that most clays are platy is extremely important in determining the magnitude of their plastic properties. It means that particle orientation is readily produced by relatively weak forces, but once a partial orientation has been achieved much greater forces are needed to disrupt the structure formed. The cohesion between parallel plates separated by a film of liquid is proportional to the square root of their contact area and inversely proportional to the thickness of the water film.

The data of Winterkorn and Moorman (21) on the Putnam subsoil, which is largely beidellite plus silt, illustrate the variations in a number of physical properties with variation in the exchange cation. In the series H, Na, K, Mg, Ca, Al, the lower plastic limit changed little but the upper or liquid limit varied greatly, sodium giving the highest value. Hence, the sodium soil showed the highest plastic index. Potassium was lowest, due probably to considerable fixation effects upon drying. The rest were all somewhat higher than the potassium values.

The mechanical properties of clays in the lower moisture range have been examined in some detail by Grim and Cuthbert (10). Their study of molding sands, to which varying quantities of different clay minerals plus water were added, has led them to the conclusion that the maximum (green) compression strength occurs for different sand-clay proportions at about the same moisture content per unit weight of clay. The same is true of the minimum bulk density, which corresponds to a somewhat greater proportion of water. They interpret this behavior as indicating that the physical state of the mixture corresponds to the production of immobile layers of

water molecules on the clay surfaces. Although this process, in itself, is a highly probable one, the author is not satisfied that these experiments afford good evidence of it. The authors entirely neglect any moisture films on the sand grains and, in calculating the thickness of the water films for montmorillonite, they assume that the water is uniformly distributed over all the lattice surfaces, thus arriving at the figure of three layers of water molecules for sodium montmorillonite at the point of maximum green compression strength. For illite, halloysite, and kaolinite, which have external surfaces only, the moisture contents for a coating of 3-4 water molecules would be much smaller than is actually found. It is difficult to envisage kaolinite, halloysite, and illite arriving at this point with water layers, say 20-100 molecules thick as against three for montmorillonite.

#### *Swelling*

Although swelling, strictly regarded, is an osmotic property of the clays, it can be discussed at this point because of its obvious relation to interparticle forces. It is clear that swelling may be effected in two ways—by the interposition of solvent molecules between particles, or between the lattice units which comprise the particles themselves. In the kaolinite and mica-like clays, only the former process would operate. This, however, does not lead to extensive swelling, at least not for kaolinite, while no measurements are available for the illites. With the montmorillonite and beidellite clays swelling is a very prominent property, but the experimental data do not enable one completely to separate the interparticle effects from those occurring internally. In extreme cases, indeed, the distinction between them disappears. A montmorillonite might swell in a polar liquid until it eventually dispersed into plates of unit molecular thickness. All the surface could then be regarded as external. Experiments on swelling thus display, in an extremely sensitive fashion, the factors responsible for colloidal stability in the broad sense. Table XVIII illustrates the effect of the polarity of the liquid upon the swelling of Putnam clay.

Baver and Winterkorn (3) investigated the relationship of the swelling to other colloidal properties for bentonite (montmorillonite) and Putnam clay (beidellite) saturated with various cations. Although both belong to the swelling class, very interesting quantitative differences between them were found (Table XIX). The most remarkable is the difference with respect to potassium. The potassium Putnam clay actually swells less than the calcium or barium clays. No such enormous difference between sodium and potassium is found in the *zeta* potentials nor the degree of dispersion in water. The heat of wetting, however, is considerably lower for the potassium clay than for any of the others. This strongly suggests that the fixation of potassium into a nondissociating form has been especially marked in the

Putnam clay. The clays were dried after neutralization with the respective bases. This process is known to be exceedingly effective in fixing potassium in the beidellitic clay minerals.

In carrying out experiments on the application of the Donnan equilibrium to clay systems, Mattson (14) made swelling measurements in presence of various sodium salts. The valency of the anion was shown to exert a strong effect upon the swelling of sodium bentonite, the order being ferrocyanide > sulfate > chloride. In all cases, the swelling decreased as the excess salt increased. In experiments on the neutralization of hydrogen bentonite with sodium hydroxide, a maximum in swelling occurred near

TABLE XVIII

*The Uptake of Polar Liquids by Putnam Clay in Relation to Their Dielectric Constants*  
(Winterkorn and Bayer, 20)

Liquid	Total intake cc./g.	Dielectric constant	Swelling cc./g.
H <sub>2</sub> O	0.99	78.0	0.58
CH <sub>3</sub> OH	0.66	31.9	0.25
C <sub>2</sub> H <sub>5</sub> OH	0.60	24.1	0.19
C <sub>2</sub> H <sub>5</sub> OH (n)	0.57	20.5	0.16
C <sub>2</sub> H <sub>5</sub> OH (n)	0.53	14.6	0.12
CCl <sub>4</sub>	0.41	2.2	0.00 (assumed)

TABLE XIX

*Water Intake by Bentonite and Putnam Clay Saturated With Various Cations and by Kaolinitic Cecil Clay (Bayer and Winterkorn)*

Clay	(Values in cc./g.)					
	Li	Na	K	Ba	Ca	H
Bentonite	10.77	11.08	8.55	2.50	2.50	2.20
Putnam	4.97	4.02	0.50	0.85	0.91	0.81
Cecil clay	—	—	—	—	—	0.05

the point of equivalence. This evidently corresponds to the maximum in viscosity observed in the same region for dilute sols and to the first zone of thixotropy in more concentrated systems. Fig. 74, taken from the work of Freundlich, Schmidt and Lindau (7), similarly shows how maxima in swelling and in sedimentation volume, and a minimum in thixotropic setting time, are found just before the point of equivalence on the hydrogen bentonite-potassium hydroxide titration curve.

*Swelling Pressure.* The only measurements available on the swelling pressures of clays appear to be those of Mattson (15) on sodium bentonite which extend only to one atmosphere, Woodruff's measurements on Putnam clay up to 20 atmospheres (22), and the data obtained by Norton and Lawrence for a fractionated kaolinite which range up to 60 atmospheres (18). Mattson found a linear relation between the logarithm of the swelling

pressure and the logarithm of the water held. At very low pressures, however, the gel shows a limiting volume, that is, it does not proceed to complete peptization in absence of agitation. The state attained now corresponds to a zone of thixotropy and indicates in another way that internal forces hold the system together in opposition to the osmotic forces. Mattson calculates that this internal attraction corresponds to a negative osmotic pressure of about 0.02 atmospheres for sodium bentonite, when the latter has imbibed 9–10 ml. of water/g.

The data on kaolinite clays are usually regarded somewhat differently, since these actually swell very little in contact with water. Nevertheless, the particles hold water films against considerable tensions and the experimental determinations are in principle precisely the same as measurements of swelling pressure. From their measurements on a kaolinite fraction of 0.2–0.4 $\mu$  equivalent diameter, Norton and Johnson have calculated the average film thicknesses at different pressures. They are found to range from 3.6 $\mu$  at 36 atmospheres to 34 $\mu$  at 0.3 atmosphere.

The three sets of data on bentonite, Putnam clay, and kaolinite show close similarity in general character when plotted on a double logarithmic scale as in Fig. 75. The lower parts of the curves seem to be approximately linear, and in each case there is a tendency for the slope to become less steep at the higher moisture contents. This reflects the tendency for the swelling to be limited in extent, as noted above. The connection between these data and the Verwey theory has already been discussed.

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## CHAPTER 14

### THE PROPERTIES OF CLAY AGGREGATES AND FILMS

#### *Specific Gravity and Specific Volume*

It is characteristic of the clays that the measurement of such a simple, normally well-defined property as specific gravity should lead into experimental difficulties not easily circumvented, and through them into the very center of discussion of properties depending upon structural features. From what has been said regarding adsorption, one can readily see that, in the group of internally reactive clays, the specific gravity of single clay micelle cannot be a constant. It depends upon the specific gravity of the polar liquid with which the particle is in equilibrium. Furthermore, due to molecular orientation, the liquid taken up internally may have a different specific gravity from that in bulk, the actual value depending upon the amount held under the conditions of the experiment. Even more disturbing, is the fact that, in dealing with clay films and aggregates, the behavior toward liquids is a function also of the manner in which the micelles are arranged. It is thus affected by the previous history of the material whose specific gravity is being measured. These impediments to accuracy arise in some measure with all finely divided materials, and it is not surprising that the montmorillonitic clays, with their complete molecular accessibility to polar liquids, should afford extreme examples.

Two methods may be used to secure values which can be used as reasonably characteristic constants. The first is to determine the specific gravity of the micellar particles suspended in an aqueous medium, by adjusting the specific gravity of the liquid until solid and liquid have the same value. Aqueous potassium mercuric iodide can well be used (6). In such a liquid, the exchange cation on the clay will certainly be potassium and the internal moisture content will be determined by the vapor pressure of the liquid. The latter can easily be determined for various mixtures of potassium mercuric iodide and water.

The second method involves the use of nonpolar liquids. The powdered clay aggregate is prepared in some reproducible way. It is then brought to equilibrium with water vapor under standard conditions, and is finally wetted and suspended in an appropriate nonpolar liquid. In this procedure, great care must be taken lest entrapped air remain in the powdered aggregates

The first hint of unusual complexities arose during the work of Anderson and Mattson on clay fractions prepared from various soils (1). They found that the specific gravities appeared to be higher in water than in toluene. Adsorbed water was therefore assumed to have a greater specific gravity than water in bulk.

A few years later, Russell, in a very stimulating contribution to soil physics (17), thoroughly investigated these effects in relation to the following variables: the polar character of the liquid, the nature of the exchange cation, and the exchange capacity of the clay. Unfortunately, no pure clay

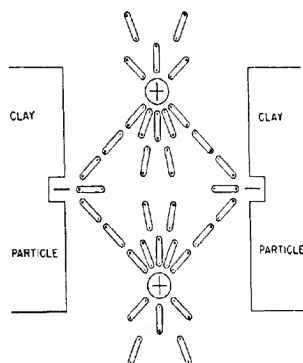


Fig. 78. Linkage between adjacent clay particles in crumb formation according to Russell.

minerals were used, but, because of the wide range of characteristics of the clay fractions employed, valid conclusions could be drawn. In order to make use of additive relationships, specific volumes were used instead of specific gravities. Using water, the effect of varying the exchange cation was first examined. It was found, for instance, that the specific volume of a potassium clay was always greater than that of a sodium clay. This difference divided by the exchange capacity gave reasonably good constancy for different clays. It agreed remarkably well with the specific volume differences for different anhydrous potassium and sodium salts. Hence, under the conditions of these experiments there was little change in hydration when sodium was substituted for potassium. Other pairs of ions, however, showed considerable differences, the calcium and magnesium clays being more hydrated than the sodium and potassium clays. In polar liquids, including water, the specific volumes were significantly less than in nonpolar



liquids (tetrahydronaphthalene was taken as standard), but there was no clear relationship to the dipole moment.

Hauser and Le Beau (3) have determined the specific gravities of a number of bentonite fractions in water at different concentrations. In agreement with Mattson and Russell the limiting values at high clay concentrations are higher than those found in a nonpolar liquid. They find, however, that at low concentrations much lower apparent values are obtained, and that, as the particle size decreases, the apparent specific gravity increases. Their explanation of these peculiar results is not convincing. They suppose that the lower concentrations involve greater hydration and therefore greater compression of the adsorbed liquid than the higher concentrations. Since, however, all experiments showed that the main differences occurred below 0.5% clay concentration, this idea seems unwarranted. The author believes that the discrepancies are largely due to differences in the clay films which were finally produced and weighed after evaporation of the liquid. At a given temperature of drying very variable moisture contents can be found in such films depending upon their precise mode of formation (see below).

#### *Hydration Properties*

Numerous workers have participated in dehydration studies of the clays, and over a period of years it has become generally recognized that, in order to obtain reproducible results, a well defined procedure for the preparation of the samples must be adhered to. The clay is usually dried at room temperature, ground, sieved through a fine screen, and finally brought to equilibrium in an oven or furnace at various temperatures.

In attempting to obtain dehydration curves for various fractions of the clay minerals nontronite, attapulgite, and hectorite (saponite), Caldwell and Marshall (2) used very small quantities, prepared as thin films upon crucibles or dishes by the evaporation of dilute suspensions. Up to quite high temperatures these films retained water much more tenaciously than powdered clays. It was not so much a matter of sluggishness in attaining equilibrium as of a permanent increase in moisture content. Table XX gives the 110°C. values, both in powdered and film form. The differences are large. Figure 81 illustrates the persistence of this effect up to high temperatures, the data for powdered hectorite being taken from the work of Nutting (15).

The explanation seems to lie in the fact that clay films prepared by slow evaporation possess a considerable degree of orientation caused by the anisotropic character of the particles. In studying a clay film, we have superimposed upon the moisture relationships of the individual particles, a new set belonging to the structure. The latter is formed, in many instances, by a parallel orientation of plates or laths. In the removal of water,

these units can probably approach each other as closely as do the individual lattice units in the "expanding lattice" clays. Thus, the dehydration of a clay film will be enormously affected by the conditions which operate during its formation and which determine the extent and perfection of the orientation of the clay particles. Water held within the micelles (OH groups perhaps excepted) and film structure water become finally indistinguishable, being held by bonding energies of the same order of magnitude.

These factors were probably largely responsible for the peculiar results obtained by Hauser and Le Beau (4) in their study of film formation by sodium montmorillonites of different particle sizes. They found that films prepared from the finest fractions held the least water. However, after

TABLE XX  
*Moisture Content at 110°C. (Ignited Basis) of Clay Fractions in Relation to the Type of Aggregation*

Clay	Fraction	Water held at 110°C.	
		Powder	Film
Nontronite	2- 1 $\mu$	14.7	20.8
	1 $\mu$ -500 m $\mu$	16.8	22.7
	200- 50 m $\mu$	19.9	22.5
Attapulgit	500-200 m $\mu$	20.1	24.6
	200- 50 m $\mu$	18.4	24.0
Hectorite	2 $\mu$ - 1 $\mu$	16.2	29.3
	1 $\mu$ -500 m $\mu$	15.3	26.0
	200 m $\mu$ - 50 m $\mu$	12.6	24.4

heating to temperatures between 110° and 450°C. and exposing to water vapor, all fractions came to equilibrium at the same moisture content. Heating caused a shrinkage of the film, in the course of which the original differences in structure practically disappeared. This strongly suggests that the distinction between inter- and intraparticle water had also vanished.

#### *Mechanical Properties*

*Crumb or Aggregate Formation.* The work of Russell, previously referred to (17), gave valuable qualitative data on the strength of clay crumbs prepared in various ways. The kaolinite clays with low exchange capacity did not form stable crumbs, whereas other clays with a high exchange capacity did. Particles  $> 2\mu$  did not form stable aggregates; below this size, the smaller the particles the greater was the strength of the crumbs. As regards liquids, only those with appreciable dipole moments formed definite aggregates. Small exchange cations gave stronger crumbs than large organic cations. The stability of crumbs to subsequent wetting varies with the exchange cation. Thus, sodium clay aggregates are unstable in water but

stable in amyl alcohol; calcium clay aggregates are stable in water but unstable in amyl alcohol.

Electron micrographs, presented by Shaw (18), of calcium bentonite dried from water and from benzene (Jackson), show very distinct differences in the mode of aggregation (Figs. 79, 80). The material dried from benzene seems to take the form of well oriented packets of plates, whereas that from water shows the usual random arrangement of flat plates of varying thicknesses. The two preparations had different X-ray characteristics also. That from water gave a weak 15 Å and a 10 Å spacing, that from benzene a well



Fig. 79. Montmorillonite dried from water. (Shaw.) Electron micrograph by Jackson.

defined 15 Å spacing only. Thus, the distribution of spacings as well as the mode of aggregation are affected by the previous history of the sample.

*Film Formation.* It was shown by the work of Hendricks and Fry (5) that thin films of clay, produced by evaporation on microscope slides, displayed optical properties clearly indicative of orientation. Not only did it appear that thin plates arranged themselves parallel to the surface of the slide, but a measure of orientation within this plane was apparent from the biaxial interference figures sometimes obtained. Ross and Hendricks (16) point out that, in certain clay deposits, notably the gouge clays, the optics indicate very perfect orientation.



Fig. 80. Montmorillonite dried from benzene. (Shaw.) Electron micrograph by Jackson.

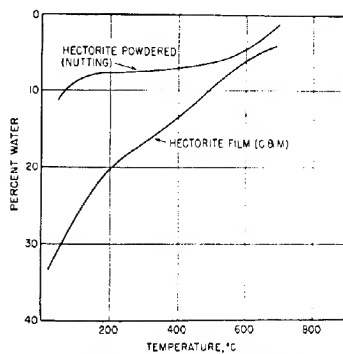


Fig. 81. Effect of film formation upon the moisture content of hectorite at various temperatures.

Hauser and Le Beau have studied the foundation of partially oriented aggregates and their coalescence upon drying to give mechanically stable films of bentonite (4). These films are now produced commercially under

various patents. By varying the exchange cation it is possible to change the mechanical properties, to give the films greater or lesser flexibility and tensile strength. It is noteworthy that potassium and lead clay films produced by base exchange from the original sodium clay films are coherent in presence of water. The sodium clay films are not; they swell, crack, and eventually disperse. The ionic sizes of potassium and lead are not widely different; probably both are fixed in nonexchangeable form by montmorillonite clays. Hence, they are able to bind lattice units together on drying so that subsequent attack by water molecules can no longer cause disruption.

#### *The Electrochemical Properties of Clay Films*

Since 1940 much time and effort have been devoted by the author and his associates to the investigation of clay films. The reasons for this highly detailed study lay in the fact that it seemed possible to use them as membrane electrodes, permeable to cations but not to anions. Hence by simple potentiometric measurements one might hope to determine single cationic activities in solutions and in colloidal sols. Eventually, perhaps, even the analysis of cationic mixtures might be attained. The widespread use of the glass electrode for the measurement of pH values had encouraged speculation regarding membrane electrodes by which other cationic activities could be measured. The biologists, and soil scientists in particular, greatly needed information on sodium, potassium, ammonium, calcium, and magnesium, none of which can be estimated in low concentration by amalgam electrodes. The author's investigation of plates ground from zeolitic crystals (Chapter 3) showed that the quest was not hopeless. The preparation of clay films by Hauser and Le Beau prompted an examination of their electrochemical properties. These proved to be moderately favorable, the main difficulty being the lack of strength and stability in contact with water. This was remedied by preliminary heat treatments, which, provisionally enough, improved also the electrochemical properties (7).

During this investigation, membranes were compared with one another by using a theory of permeable membranes developed independently by Teorell (19) and by Meyer and Sievers (13). This theory has provided a quantitative basis for their electrochemistry. Actually, our clay membranes are not permeable in the sense envisaged by these authors. Nevertheless, their quantitative behavior is largely controlled by factors which they were the first to recognize. We shall therefore outline the Teorell-Meyer and Sievers theory before showing how it must be modified to deal with the case of the clay films.

*Teorell-Meyer and Sievers Theory for Porous Membranes.* Consider a negatively charged membrane in contact with two solutions of the same salt at different concentrations. With renewal of the solutions cation exchange will occur until the ions which balance the negative charge of the

membrane become the same as those in the solutions. If, for example, the salt is sodium chloride, we then have the situation presented in Fig. 82, the membrane being magnified in thickness. Hypothetically the latter can be divided into three zones A, B, and C. In zones A and B there is set up a Donnan equilibrium. Here the equilibrium concentrations of cation and anion can readily be calculated if a definite value is given to A, the mean activity of the cations associated with the membrane itself. It is assumed that A remains unaffected by changes in the activities of the sodium ions in the outer solutions. The formulae are given in the figure. Correspondingly, two potentials  $E_1$  and  $E_2$  are set up. The third zone C is the site

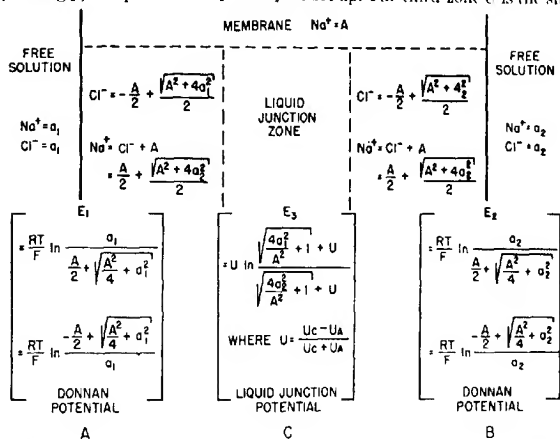


Fig. 82. The three zones in a negatively charged porous membrane according to the Teorell-Meyer and Sievers theory.

of a diffusion junction between the ions present in A and those in B. By applying Henderson's equation for the liquid junction potential to this special case,  $E_3$  can be evaluated.

The final equation for  $E_1 + E_2 + E_3$  can be written in the form

$$E_{\text{Membrane}} = \frac{RT}{F} \left[ \frac{1}{2} \ln \left( \frac{\left( \sqrt{\frac{4a_2^2}{A^2} + 1} + 1 \right) \left( \sqrt{\frac{4a_1^2}{A^2} + 1} - 1 \right)}{\left( \sqrt{\frac{4a_1^2}{A^2} + 1} - 1 \right) \left( \sqrt{\frac{4a_2^2}{A^2} + 1} + 1 \right)} \right) + U \ln \frac{\sqrt{\frac{4a_1^2}{A^2} + 1} + 1}{\sqrt{\frac{4a_2^2}{A^2} + 1} + 1} \right]$$

where the first term is  $E_1 + E_2$  and the second term is  $E_3$ . The symbol  $U$  in the expression for the liquid junction potential represents  $\frac{U_c - U_A}{U_c + A_A}$  where  $U_c$  is the mobility of the cation of the salt in water and  $U_A$  is that of the anion. It is assumed that the values are not affected by changes in concentration, and that the Na ions associated with the membrane have the same mobility as those belonging to the NaCl. When a salt like KCl is chosen, for which  $U_c = U_A$  this liquid junction potential  $E_3$  disappears. It can readily be seen that if  $A$  is large compared with  $a_1$  and  $a_2$ ,  $E_3$  again becomes negligibly small compared with  $E_1$  and  $E_2$ . The sum of the latter then approaches the limiting value  $\frac{RT}{F} \ln \frac{a_1}{a_2}$ . In other words, irrespective of the nature of the salt or the membrane, the latter acts in the limiting case as a cationic sieve and the Nernst equation is obeyed.

It is evident, however, that high values of  $A$  can only be obtained by materials having large numbers of dissociated cations per unit volume; in other words, the base exchange capacity times the fraction of cations dissociated must be high. Secondly, the pore structure must be essentially homogeneous, otherwise a few large pores might contain liquid in which  $A$  was not large, and so provide conducting channels characterized by much lower potentials than those of the finer pores.

To make use of so complex an equation as that quoted above, graphical methods are employed. The value of  $A$  and the ratio  $\frac{a_1}{a_2}$  are first arbitrarily fixed to reduce the number of variables. Then the potential  $E_{\text{membrane}}$  is plotted against  $-\log a_2$  for different assigned values of  $U$ . When this is done, a family of curves results (Fig. 83). If now a different value of  $A$  is chosen, a second family of curves is obtained exactly similar to the first but displaced along the  $-\log a_2$  axis by a distance corresponding to  $-\log A$ . Thus, in investigating a membrane, the experimental curve for  $E_{\pi}$  got by keeping  $a_1/a_2$  constant and varying  $a_2$  can be compared with, say, a family of curves for which  $A = 1$ . The experimental curve should fit one of the theoretical curves simply by displacing it along the axis a distance corresponding to  $-\log A$ . Hence  $A$ , an important characteristic of a membrane, can be determined. Furthermore, suppose the experiment has been carried out with a salt having anion and cation of equal mobilities in water. Then, as far as pure theory is concerned, the experimental curve should also follow this condition, that is, it should correspond to the theoretical curve for  $U_c = U_A$  or  $U = 0$ . However, many membranes depart considerably from this condition. They exert a sieve action, restraining large ions more than small ones. In such cases, the experimental curve for potassium chloride (equal mobilities of anion and cation) will not correspond to the theoretical

curve for  $U_c = U_A$ , but to some other member of the family. Generally  $U_c > U_A$ , since metallic cations are commonly smaller than associated anions. In this sense  $U_c/U_A$  gives a measure of the sieve action.

The theory of Teorell and of Meyer and Sievers thus provides two measures which control the electrochemical properties of porous membranes;

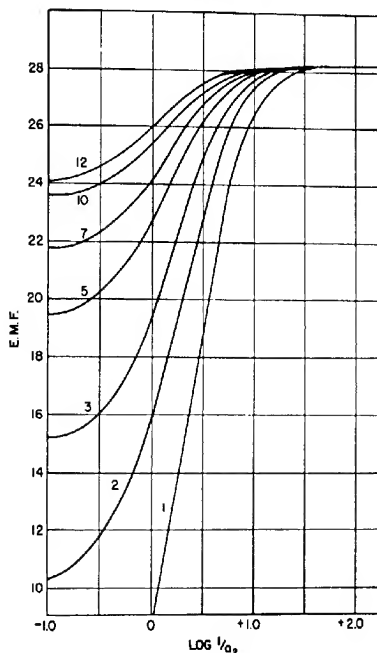


Fig. 83. Theoretical curves according to the T, M & S theory for E. M. F. against  $\log \frac{1}{a_2}$  when  $\frac{a_1}{a_2} = 3.00$ ,  $A = 1.00$  and  $\frac{U_c}{U_A}$  takes on various values from 1 to 12.

$A$ , sometimes called the selectivity constant, and  $U_c/U_A$  for KCl which gives a measure of the sieve action. However, before these quantities can be derived from the measurements, it must be shown that the experimental and theoretical curves are in accord. For clay membranes this is seldom the case. Different parts of the experimental curves correspond to different values of  $A$  and of  $U_c/U_A$ . This is not altogether surprising. One assump-



tion made in deriving the theory was that  $A$  is unaffected by the external electrolyte. If, however,  $A$  corresponds to an ionic activity, it should certainly be affected, and in general diminished, by the presence of a salt with a common cation. The experimental curves appear to show this effect. If values of  $A$  and of  $U_c/U_A$  are to be deduced from them, then only the upper parts corresponding to small values of  $a_1$  and  $a_2$  should be used (Fig. 85).

The theory has been outlined for monovalent cations. It is important also to consider its application to other cases. For comparison with potas-

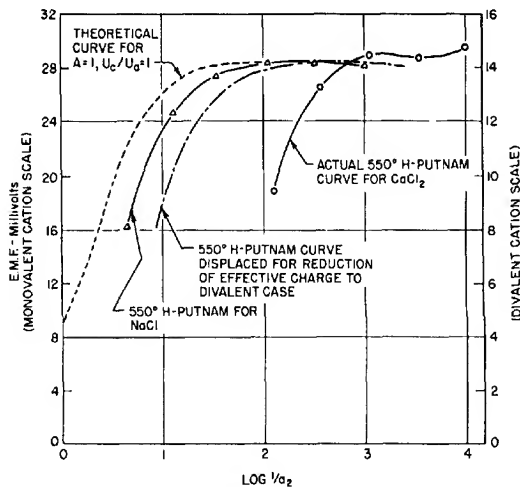


Fig. 84. Comparison of divalent and monovalent cations as regards potentials attained with the same membrane.

sium chloride, we shall take a hypothetical salt of a divalent cation with a divalent anion for which  $U_c = U_A$  in water. The ionic activities are always expressed in molality; hence, the charge on the membrane is now  $A/2$  instead of  $A$ . The effect of this is to shift the family of curves over to the right and at the same time to reduce the asymptotic maximum of the curve to one-half the value of monovalent cations (Fig. 84). Hence, if a given membrane material is to be used for determining divalent cations, the maximum permissible concentration will be considerably lower than for monovalent cations.

This, however, is not the only reason why divalent cations push the

range of usefulness for the determination of cationic activities down to lower concentrations. In general, divalent ions are much less dissociated from clay surfaces than monovalent; hence, the effective charge  $A$  will be smaller on this account. Similarly, when hydrogen is compared with the alkali metal cations, since hydrogen clays are much less dissociated than sodium or potassium clays, the range for quantitative determinations is pushed to lower concentrations.

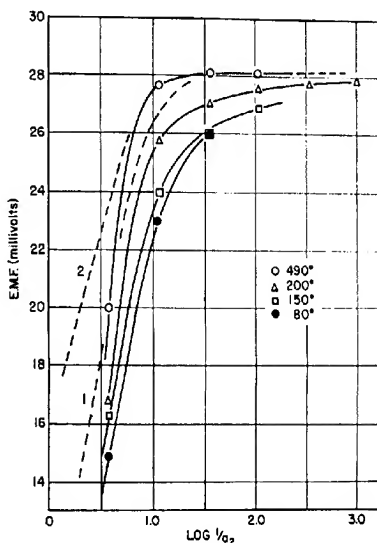


Fig. 85. Effect of preliminary heat treatments upon the electrochemical properties of hydrogen bentonite membranes toward potassium chloride. (Marshall and Bergman.)

*The Effect of Heat Treatments on Membrane Properties.* The preliminary heat treatments produce interesting changes in the properties of membranes prepared from montmorillonitic clays which are entirely in accord with the idea that intra- and interparticle spacings become largely indistinguishable. Three important factors in the final electrochemical properties are: the temperature of pretreatment, the mineralogical nature of the clay, and the exchange cation. Possibly particle size is also important, but it has not been investigated. The properties affected are: the resistance, which increases with increasing temperature of pretreatment, the charge  $A$  which also in-

creases, and the nature of the sieve action. The latter not only affects the apparent values of  $U_c/U_A$ , but in certain cases imposes a high degree of selectivity among the cations themselves.

In the case of montmorillonite (Wyoming bentonite membranes, fraction  $< 200 \text{ m}\mu$ ) the hydrogen clay membranes are somewhat different from the calcium and potassium clay membranes. Each shows a rise in resistance and in the  $A$  value with increasing temperature. As far as potassium chloride is concerned, the curves are very similar up to  $450^\circ\text{C}$ . From this point onward, however, the hydrogen clay membranes are quite different from the others. Their resistance increases up to 1–10 megohms between 400 and  $500^\circ\text{C}$ ., so that it becomes necessary to employ an amplifier for accurate results. A high degree of selectivity toward cations other than potassium also appears. Membranes prepared at  $490^\circ\text{C}$ . are practically insensitive to divalent cations, so that potassium can be accurately determined in the presence of moderate amounts of calcium or magnesium. The corresponding calcium and potassium montmorillonite membranes do not show this property. Their resistance remains below 0.1 megohm and they are sensitive to divalent ions. Indeed  $500^\circ\text{C}$ . calcium bentonite membranes can well be used to determine calcium activities in the absence of other cations (7, 8).

Beidellite membranes (prepared from Putnam clay, fraction  $< 200 \text{ m}\mu$ ) show closely similar properties for the hydrogen and calcium systems up to relatively high temperatures. In all cases below  $750^\circ\text{C}$ ., the resistance is less than 1 megohm and the estimated  $A$  values remain below 0.6. At  $900^\circ\text{C}$ . mineralogical changes occur and the resistance becomes very high. All the beidellite membranes used were sensitive to mono-, di- and trivalent ions.

*The Meaning of Cationic Mobility Ratios.*<sup>1</sup> Long before the Teorell-Meyer and Sievers theory was developed, Michaelis and his collaborators had investigated the electrochemical properties of dried collodion membranes (14). They were treated as porous, one consequence of this being that the formulae for liquid junction potentials could be applied to them. Thus, for cases in which the membrane separated solutions of sodium chloride and potassium chloride, it was seen that, if the chloride ion were assumed to have negligibly small mobility through the membrane, then the potential measured was a function of the ratio of the mobilities of the two cations.

The equation is  $E = \frac{RT}{F} \ln \cdot \frac{a_{\text{Na}}}{a_{\text{K}}} \cdot \frac{U_{\text{Na}}}{U_{\text{K}}}$  the respective ionic activities being  $a_{\text{Na}}$  and  $a_{\text{K}}$ , and their effective mobilities through the membrane  $U_{\text{Na}}$  and  $U_{\text{K}}$ . Michaelis showed that such ratios in membranes could be quite different from the corresponding values in water. A membrane could be characterized by a series of these ratios, which are readily determined using

<sup>1</sup> The term mobility ratio was used by Michaelis, but he recognized later that this quantity is more exactly described as a transport number ratio.

known concentrations of the two salts. A number of mobility ratios have now been experimentally determined for the clay membranes. It has been tacitly assumed in making such calculations that the membranes are indeed permeable (9, 10, 11).

*The Electrochemical Nature of Clay Membranes.* The first doubt over the porous nature of clay membranes arose during an attempt to set up an osmotic cell with the clay as the membrane. No movement of water was observed. Convincing proof that no real liquid junction exists inside the clay can be adduced from the potentials observed when pure hydrochloric acid solutions of different concentrations are separated by the membrane. It is then found that the potentials observed are in some cases not only lower than would be predicted from the Nernst equation, but also lower than a simple liquid junction would afford. Attack upon the membranes by the acid does not serve to explain this result, since after acid treatment they gave the same potentials when separating potassium chloride solutions as they had done previously. The low results with hydrochloric acid solutions can readily be explained if the membranes are supposed to be essentially impermeable to the solutions with which they are in contact. Thus, no true liquid junction exists within the membrane, and the potential is reduced to  $E_1 + E_2$ . Ionic movement and equilibrium are not attained in capillaries containing free solvent, but rather by the process of surface diffusion and replacement. The controlling factors within the membrane will be the energy changes associated with this replacement of one ion by another. Hence, the potentials observed should afford a measure of these energy changes, provided, of course, that the experiments are carried out at such low concentrations that the Nernst equation would be obeyed if only one salt were used.

This line of reasoning, when quantitatively applied, then leads to the following equation for the simple case discussed above, in which the membrane separates a potassium chloride solution of potassium ion activity  $a_K$  from a sodium chloride solution of sodium ion activity  $a_{Na}$  (12).

$$E = \frac{RT}{F} \ln \frac{a_{Na}}{a_K} + \frac{4.19}{F} (H_{Na} - H_K)$$

Thus, by using known solutions and determining  $E$ , one can evaluate  $(H_{Na} - H_K)$ , the difference in the differential heats of adsorption of sodium and potassium ions upon the membrane.

Thus, according to the choice of our membrane theory, we arrive at two different measures of ionic behavior in the interior of the membrane. If the membrane is porous, then its behavior toward two cations at low concentrations can be expressed by the ratio of their effective mobilities. If it is not porous, then a better measure is afforded by the difference in the differ-

ential heats of adsorption. Both measures are derived from the same type of determination and the choice as to which is the more appropriate can only be made on the basis of other evidence. As we have seen, our clay membranes are nonporous in the gross sense, yet the low potentials obtained for moderately concentrated solutions indicate that  $U_C$  is not indefinitely large compared with  $U_A$ , as it is, for instance, in the case of the glass electrode. Qualitatively at least, the membranes behave as though there is no liquid junction in the interior, yet at the surfaces the conditions are still governed by the Donnan equilibria. Hence  $A$ , the effective charge per unit volume of the membrane, continues to be of importance, although its determination leaves much to be desired.

TABLE XXI  
*Cationic Mobility Ratios and Differences in Differential Heats of Adsorption for Clay Membranes*

Clay	Temperature of pretreatment °C	Sodium-potassium	
		$U_{Na}/U_K$	$(H_{Na} - H_K)$ cal.
H—Bentonite	350	2.19	465
	450	3.80	794
H—Putnam	600	2.60	565
		Magnesium-calcium	
		$U_{Ca}/U_{Mg}$	$(H_{Ca} - H_{Mg})$
H—Bentonite	300	1.31	164
	400	1.57	268
H—Putnam	510	1.43	215
	595	1.47	227

In Table XXI some of the mobility ratios, and, corresponding to these, the differences between the differential heats of adsorption are tabulated for various pairs of cations. In general, it has been found that where monovalent-monovalent or divalent-divalent cation pairs have been employed, the values show little variation with concentration. Attempts to determine monovalent-divalent mobility ratios have revealed considerable variability. It is only in cases where reasonable constancy is found, that simple analytical methods for dealing with mixtures of cations can be developed.

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*Example:* Alexander, J., 154 (ref. 9), 164, indicates that this author's article is reference 9 on page 154, while numbers in italics refer to the page at the end of each chapter on which the references are listed.

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